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CONTENTS

	PAGE
Telecommunications in the Petroleum Industry. By Z. Friedberg	309
An Accurate Microviscometer. By Erica Glynn and L. Grunberg	331
The Use of Zinc Alkyls in the Preparation of Hydrocarbons with a Quaternary Carbon Atom. By F. R. Buck, B. B. Elsner, E. J. Forbes, S. H. Morrell, J. C. Smith, and E. R. Wallsgrove	339
Obituary: H. E. Medlicott, D.S.O.	370
Abstracts	121A
Books Reviewed and Received	143A
Applications for Membership or Transfer	i

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TELECOMMUNICATIONS IN THE PETROLEUM INDUSTRY.

Z. Friedberg *

Summary.

A general description of modern communications systems involved in the operation of oil companies. The basic principles essential for securing reliable communications and signalling under conditions generally encountered in this sphere of activities are outlined.

Introduction.

The field of application of telecommunication principles in the petroleum industry is very wide. During construction and operation of pipelines, oilfields, refineries, during pumping, loading, and refining and the multitudinous operations associated with these activities, a reliable communication service is of prime importance. It is, therefore, the aim of most of the oil companies engaged in these activities to construct and maintain their own telephone and telegraph systems, and in this article an attempt is made to describe the work which devolves upon the communications engineer in the service of an oil industry.

Fig. 1 illustrates diagrammatically the potential communication requirements of an oil company. The diagram is based on a typical large-scale organization but the same principles may be applied to an oil concern of any size.

It need hardly be said that, in an oil company, what is considered of primary importance are the oil operations proper, to which all other services within the company must adapt themselves. Consequently, the communications engineer in the service of an oil concern finds himself confronted with problems which call for solutions different from the general trend and practice of public-telephone administrations. The communications system, in order to fulfil its purpose, must be so devised as to ensure a reliable and satisfactory operation, even by unqualified staff, under very difficult conditions.

The primary considerations in deciding on an equipment for an oil company are, first, reliable and efficient operation and secondly, simplicity. The reliability of the service is of vital importance since the system is to carry important traffic. An efficient communications system is indispensable for the safety and smooth operation of the pumping, loading, or refining activities and it is of great importance that most of the traffic be cleared with the minimum of delay. Simplicity is essential in order to avoid unnecessary complication in the equipment and to enable an unqualified staff to intervene in cases of faults.

It is obvious that this can be accomplished in more than one way and we propose to examine the various alternative methods.

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* Transmission Engineer, Iraq Petroleum Company, Ltd.

Wireless Communication.

General Considerations.

Despite its many virtues wireless communication can hardly be chosen as the only means of communication for the following reasons : difficulty of retaining privacy, necessity for constant attendance of qualified operators to regulate power levels and tuning, frequent static and other interferences, and the restriction of holding conversations from places other than those where wireless equipment and aerials are located.

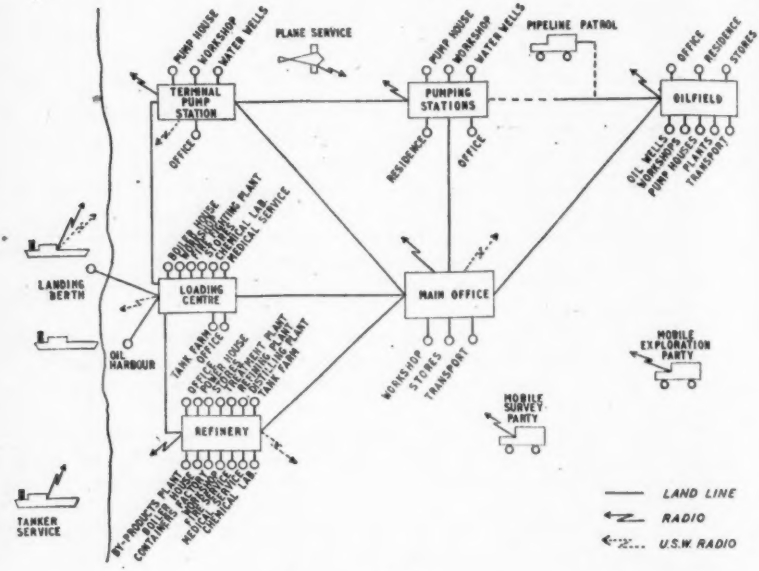

Fig. 1.

Despite these drawbacks wireless communication finds its own field. As may be seen from Fig. 1, it is used for inter-communication with tankers at sea, company aeroplanes in flight, exploration parties, and may also be considered as a communication channel of a complementary nature to land-line circuits. In this capacity it will prove particularly valuable during complete breakdowns of land-lines by either malicious or natural causes such as storms, floods, fires, etc.

Wireless can also be resorted to, as the only means of communication, in areas where the construction of land-lines is impracticable or uneconomical, such as marshy districts, etc. For this purpose a particularly useful adjunct is the ultra short-wave radio system comprising the band of frequency spectrum between 300 and 30 megacycles (1 to 10 metres). Within this band the wave-propagation conditions are particularly suitable for a reliable 24-hr communication service, provided that the transmitting

and receiving aerials are within optical sight of one another. Under suitable conditions this distance may even be exceeded in practice.

Planning.

Frequency and Power Allocations : The first step necessary to be taken when planning a wireless communication service is to ascertain what frequencies will be available for the service. The allocation of frequencies in the radio spectrum is governed by international conventions, and restrictions in regard to certain wavelengths are sometimes also imposed by local authorities. These restrictions must be known before any final decisions are made.

Radio frequencies are sub-divided into low frequencies (LF), medium frequencies (MF), high frequencies (HF), and ultra-high frequencies (UHF). Physically there is no definite distinction between any of them, nor is there any internationally accepted classification of waves in existence. However, following the latest sub-division recommended by the C.C.I.R. the writer has prepared Table I summarizing the general peculiarities of the different classes of waves for the benefit of the reader not intimately acquainted with this subject. This table gives a general idea of the behaviour of the different waves. The ranges will be affected by the location of the stations and the nature of the intervening country. They will also vary with the output power of the equipment and will depend upon the ratio of the wanted signals to the strength of the unwanted noises.

The field strength at a receiving station, distant d miles from a transmitter, radiating on a power level of P kilowatts, can be computed with reasonable accuracy with the aid of one of the numerous formulae now available for determining field-strength intensities. The expansion of the radio-communication technique has given rise to a great number of these formulae and the literature on the subject, though already very large, is continually increasing. Most of these formulae are empirical but sufficiently exact for practical calculations. The most useful practical formulae have been compiled in Table II. The table gives also the assumptions on which the validity of these formulae has been based and their practical limitations.

With the aid of a preliminary calculation of the field strength an estimate can be made of the amount of power required in the transmitter and the distance this power will cover. One of the points to remember is the importance of the aerial height (h). The field strength, which is proportional to $\sqrt{P}$, is also directly proportional to h. Hence, a doubling of h will have the same effect as quadrupling the power output. This does not apply to the same extent to receiving aerials where an excessive increase of the aerial's height will also contribute to an increase of the strength of noises and unwanted signals.

Aerials.

Vertically grounded aerials, in the form of inverted L or T, are almost essential as transmitting and receiving aerials for frequencies below 600 kc. For higher frequencies (short waves) and where directivity is not desired, the simplest type of transmitting aerial is the dipole or half-wave aerial, which may be either of the vertical or horizontal type. The horizontal

TABLE I.

Classification.	Frequency.	Wavelength.	General peculiarities.
VLF (very low freq.) .	Below 30 kc	10,000 m and above	Engineered on ground wave radiation only. The lower the frequency, the greater the range; may exceed 10,000 km. Subject to strong interference from atmospheric disturbances. High aerials required for efficient service. Not suitable for mobile service.
LF (low freq.) . .	30–300 kc	1000–10,000 m	
MF (medium freq.) .	300–3000 kc	100–1000 m	Ground- and sky-wave radiations. When engineering service, no dependence should, if possible, be made on sky-wave radiation. Ground-wave radiation very consistent at all times for 200–1000 metres. Sky-wave radiation negligible during day time, but appreciable after sunset and will provide reliable communications over great distances. For frequencies lying between 300 and 600 kc ground range will provide reliable service up to 1000 km; for 600 to 1500 kc sky-wave strength will exceed ground wave over 100 km but unreliable. For 1500 to 3000 kc ground wave used for short distances only. Atmospheric interference will increase with wavelength. Very suitable for overland service and for more purposes; particularly suitable for companies operating over mountainous and forested territories.
HF (high freq.) . .	3–30 mc	10–100 m	Sky-wave radiation of most importance. Ground wave of little use over 80–100 km. Not possible to formulate ranges for sky-wave radiations; these will depend on actual wavelength, time of day or night, season of the year, angle of radiation, etc. When average conditions prevail, ranges may be predicted for a given frequency and time from available data. In general, sky-wave radiations of wavelengths below 70 metres will exceed 1000 km. More than one frequency will be required for 24-hr service. Daylight transmission improved with increased frequency. Requires very little power and comparatively small aerials. Subject only to interference from local storms and other local man-made statics. Skip distance will depend on wavelength, season, and local time; will increase with frequency and will be greater in night and in winter.
VHF (very high freq.)	30–300 mc	1–10 m	Ground-wave propagation within optical horizon (line-of-sight). Under suitable conditions range may exceed considerably line-of-sight distance but, when engineering equipment, no dependence should be made on ranges exceeding by 10 per cent optical distance. Within this distance, the service will meet very closely all the desiderata of a high grade physical-communication circuit, viz., consistent and reliable day and night communications, absence of fading and interference (except from local ignition systems). Requires very little power, comparatively simple and small equipment and small aerials (dipoles). May also be used on mobile stations.

IDEAL CASE
(Hertzian Formula)

$$E_0 = \frac{300\sqrt{p}}{d}\left(\frac{mv}{m}\right)$$

ASSUMPTIONS

1. Flat Earth, perfectly conducting and space of same nature in all directions (no absorption).
2. Vertical Aerial.

LIMITATIONS

Valid for very short distances, but greater than a few wavelengths ($d > 5\lambda$).

Vertical $\frac{\lambda}{4}$ Aerials.

DIRECT GROUND WAVES

Austin-Cohen's Formulæ.

(1911) | (1926)

$$E = E_0 f_1(\lambda d)\left(\frac{mv}{m}\right), \quad E = E_0 f_2(\lambda d)\left(\frac{mv}{m}\right)$$

$$f_1(\lambda d) = e^{-0{\cdot}0015\frac{d}{\lambda^{3/2}}}$$

$$f_2(\lambda d) = e^{-0{\cdot}0014\frac{d}{\lambda^{3/2}}}$$

ASSUMPTIONS

Transmission over sea-water with Earth's curvature neglected.

LIMITATIONS

1. Applicable to oversea transmission, more accurate results for daylight transmission.
2. $\lambda > 500$ m.
3. d . . . 500–8000 km.
4. Accuracy increased with distance.

Watson's Formula (1919)

$$E = E_0 f_3(\lambda d)\left(\frac{mv}{m}\right)$$

$$f_3(\lambda d) = 0{\cdot}1136\frac{d^{0{\cdot}5}}{\lambda^{1/3}}e^{-0{\cdot}00076\frac{d}{\lambda^{2/3}}}$$

ASSUMPTIONS

1. Spherical Earth perfectly conducting.
2. Atmospheric refraction neglected.
3. Attenuation due to diffraction effect only. (Attenuation due to Earth's finite conductivity is neglected.) Assumption valid for larger distances.

LIMITATIONS

1. Valid for $d/\lambda^{1/3} > 160$.
2. Satisfactory results for:
   d = 500–3000 km.
   λ = 500–2000 m.

Burrow's Formula (based on Watson's).

$$E = E_0 f_4(\lambda d)\frac{mv}{m}, \quad E = E_0 f_5(\lambda d)\frac{mv}{m}$$

$$f_4(\lambda d) = (1 + 2x)^{0{\cdot}5}e^{-x}$$

$$x = 0{\cdot}0035\frac{d}{\lambda^{1/3}}$$

$$f_5(\lambda d) = (1 + 2x')^{0{\cdot}5}e^{-x'}$$

$$x' = 0{\cdot}0029\frac{d}{\lambda^{1/3}}$$

1. Valid for distances up to 10,000 km.
2. Good approximation over sea-water for $\lambda > 450$ m., but may also be used for over-land transmission.
3. $E_r = E_0 f_6(\lambda d)\frac{mv}{m}$ corrected formula for refraction effect; to be taken into consideration for $\lambda < 600$ m.

Van der Pol's Formula (1931)

(simplified Sommerfeld's classical solution).

$$E = E_0 f_6(\lambda d\delta)\left(\frac{mv}{m}\right)$$

$$f_6(\lambda d\delta) = \frac{2 + 0{\cdot}3p}{2 + p + 0{\cdot}6p^2}$$

p ("numerical distance")

$$= \frac{\pi \cdot 10^{-15}d}{6\lambda\delta} \text{ emu}$$

for $p > 10$

$$f(x_0) \simeq \frac{1}{2p}$$

(sufficient approximation)

ASSUMPTIONS

1. Imperfectly conducting flat Earth.
2. Attenuation considered due to dissipation of energy by Earth's finite conductivity. (Diffraction effect neglected.)
3. Displacement current, *i.e.*, dielectric constant of Earth neglected (Earth assumed to be resistive only).

LIMITATIONS

1. Satisfactory for daylight transmission.
2. Applicable to sea and land for:
   λ = 200–2000 m.
   d = 200–2000 km.
   with improved accuracy for $d < 1000$ km.

INDIRECT SKY WAVES

Medium and long waves.

Austin's Formula (1926)

$$E = E_0 f_7(\lambda d)\left(\frac{mv}{m}\right), \quad E = E_0 f_8(\lambda d)\left(\frac{mv}{m}\right)$$

$$f_7(\lambda d) = \sqrt{\frac{\theta}{\sin\theta}}e^{-46{\cdot}10^{-6}d/\lambda^{0{\cdot}5}}$$

$$f_8(\lambda d) = \sqrt{\frac{\theta}{\sin\theta}}e^{-4{\cdot}10^{-6}d/\lambda^{0{\cdot}5}}$$

ASSUMPTIONS

1. If no high precision is required.

LIMITATIONS

1. Valid only for $\lambda > 300$ m $f(x_0)$ based on Transatlantic transmission data for 17–60 kc.

Anderson and Bailey (1926)

No formula in practical form available (see article on Short Waves, by T. L. Eckersley, in *J.I.E.E.*, June 1927, for formula based on ionic refraction). Reasonable forecast possible from available experimental data when normal conditions prevail.

Short waves

DIRECT GROUND ULTRA-SHORT WAVES

Within optical Sight (Range of Vision)

Range of vision $d = 3{\cdot}55(\sqrt{H_1} + \sqrt{H_2})$.

Range of vision with refraction effect (bending effect of rays due to Earth's curvature):

$$d = 3{\cdot}55\sqrt{\frac{m}{m-1}}(\sqrt{H_1} + \sqrt{H_2})$$

m (index of refraction) from practical observations 15 in winter and 7 in summer, average value $(15 + 7)\frac{1}{2} = 11$, equivalent to assumption that radius of Earth is increased by 4/3 (average practical range of vision under normal conditions usually 10% higher).

Dipole $\frac{\lambda}{2}$ Aerials

Trevor and Carter (1933) Norton (1937)

$$E = E_0 f_9(\lambda d\varepsilon\delta H_1 H_2)\left(\frac{mv}{m}\right)$$

For Vertical polarization (Vertical Aerials)

$$f_9(\lambda d\varepsilon\delta H_1 H_2) = \frac{10^{-3}}{d\sqrt{2}}\left[\frac{2\varepsilon_0(H_1 + H_2)}{\sqrt{\varepsilon_0 - 1}} + j\frac{4\pi H_1 H_2}{\lambda'}\right]$$

For Horizontal polarisation (Horiz. Aerials)

$$f_9(\lambda d\varepsilon\delta H_1 H_2) = \frac{10^{-3}}{d\sqrt{2}}\left[\frac{2(H_1 + H_2)}{\sqrt{\varepsilon_0 - 1}} + j\frac{4\pi H_1 H_2}{\lambda'}\right]$$

ε_0 = complex dielectric constant

$$\varepsilon_0 = \varepsilon - j\frac{18 \times 10^{09} \times \delta}{f'}$$

ASSUMPTIONS

Earth flat and uniform.

LIMITATIONS

1. Valid for $\frac{H_1 + H_2}{d} < 0{\cdot}05$

($d \gg H_1$ and H_2).

Simplified approximate formulæ

$$E = E_0\frac{4\pi H_1 H_2}{\lambda' d} \times \frac{10^{-3}}{\sqrt{2}}\left(\frac{mv}{m}\right) \quad . \quad (1)$$

(On basis of f_9 simplified)

$$E = \frac{0{\cdot}84\sqrt{10p}}{d^2\lambda'}H_1 H_2\left(\frac{mv}{m}\right) \quad . \quad (2)$$

(Burrows, Decino and Hunt)

$$E = \frac{0{\cdot}88\sqrt{10p}}{d^2\lambda'}H_1 H_2\left(\frac{mv}{m}\right) \quad . \quad (3)$$

(Petrie and Saxton)

$$E = \frac{0{\cdot}9\sqrt{10p}}{d^2\lambda'}H_1 H_2\left(\frac{mv}{m}\right) \quad . \quad (4)$$

(Norton)

LIMITATIONS

1. H_1 or H_2 = 3–25 m.
2. d = 1–50 km.

---

p = Power in kw.
d = Distance in km.
λ = Wavelength in km.

λ' = Wavelength in m.
f = Frequency in kc/s.
f' = Frequency in c/s.

H_1 = Height (physical) of transmitting Aerial in m.
H_2 = Height (physical) of receiving Aerial in m.
ε = Dielectric const. of Earth.
δ = Conductivity of Earth, emu.

ε_0 = Complex dielectric Const.
θ = Angle at centre of Earth corresponding to transmission path in radians.
$j = \sqrt{-1}$.
$e = 2{\cdot}718$.

Note.—All field strengths are expressed in $\frac{mv}{m}$ and E_0 in all cases as given by above Hertzian formula $= \frac{300\sqrt{p}}{d}$.

[*To face p.* 312.

type is sometimes preferred because of its better signal-to-noise ratio, particularly where interference is expected from ignition which is vertically polarized.

Where a certain directivity is desired, this can be obtained by the use of various types of aerial arrays of which the two-element type is the simplest. For a more pronounced directivity the rhombic type of aerials, consisting of four non-resonant wires erected in the form of a rhomboid, offer the most economical solution for a private short-wave service.

For short-wave reception, a simple 20 to 25-ft-long wire will be found quite sufficient for all purposes. However, where directivity is required, rhombic type aerials, supported by telephone (wooden) poles, will also in this case offer a suitable and inexpensive solution.

Interference.

Whilst field strength can be determined for any given power and range, the actual requirements will depend upon the relation this strength will bear to the noise level at the receiving station.

Noises are produced primarily by atmospheric disturbances, by man-made statics (machinery, ignition, etc), and by internal noises generated in the receiver itself (thermal agitation). The conventional methods of noise reduction are improved selectivity of the receiver and directive aerials. This is necessary since noise energy is usually distributed over a wide frequency range, and by improving the selectivity of the receiver, obtained by narrowing the receiver's tuning circuit, the noises lying outside the received frequencies are completely eliminated. Thermal agitation noises can only be reduced by improving the quality of the valves and the circuit, and man-made statics by the use of suppressors at the sources of noise and by screening the down-lead of the receiving aerial.

A signal-to-noise ratio of 5 db will permit a satisfactory reception on commercial-telegraph service which can often be operated with signal-field strengths as low as 1 μV/md.

For medium waves a field strength of 10 μV/m will in many cases be sufficient for satisfactory communication between two stationary stations and 50 μV/m for mobile stations.

For short waves, the compilation data prepared by the Engineering Dept. of Cable and Wireless and published in an article on " Field Strength Required for Commercial Telegraphy on Short Waves " (*Marconi Review*, May–June 1936, page 10) gives the following approximate minimum field strengths, for half-wave vertical aerials (dipoles) :—

Over 15 metres . . .	0·5 μV/m
„ 25 metres . . .	0·2 μV/m
„ 40–100 metres . . .	less than 0·2 μV/m

Equipment.

It is difficult to lay down general conditions as to which type of wireless equipment will provide the best service. This will largely depend on specific requirements of the service, local conditions, distance to be covered, etc, and there will be an individual solution for each case. No attempt is therefore made to discuss circuit details, but the essential requirements may be summarized as follows :

Transmitters : General utility type, *i.e.*, continuous wave (CW), interrupted continuous wave (ICW), and telephony. Simplicity in design and in operation and easy accessibility to all components. High degree of crystal-controlled frequency, stability, and rapid wave-change facility with spot waves, and remote control features for starting and frequency changing, if necessary.

On private systems, radio transmitters need not strictly adhere to the requirements and standards of performance of broadcasting transmitters, and can therefore be considerably simplified in design and operation.

Receivers : The circuit of a communication receiver differs to a certain extent from that of a broadcast receiver. It also usually includes a beat-frequency oscillator and other refinements such as crystal filters and noise-suppression devices. The latter is especially necessary where the receiver has to operate in the vicinity of ignition systems.

The requirements of a modern receiver can be summarized as follows: modern superheterodyne, beat-frequency oscillator, single-tuning control, high sensibility, high selectivity, efficient automatic volume-control, visual-tuning indication and, where necessary, emergency calling facilities if continuous listening is not possible.

Ultra-short-wave Service.

As already mentioned, a particularly useful and interesting adjunct to the telecommunication art is the ultra-short-wave service. For oil companies, in particular, this system offers an ideal medium for meeting communication requirements between any two comparatively short distant points (1 to 100 miles) where, for economic or other reasons, the construction of a physical telephone line would prove either impossible or impracticable. Here are a few examples of possible applications : marshy districts, between an island and the mainland replacing a submarine cable, deep-water crossings, between a tanker moored to an outlying berth and a shore station controlling the loading operations, between a tank-farm and a distant pump-house, between wells, between short-distant mobile surveying stations, between a fixed permanent station and a temporary outlying construction camp, etc.

For distances not exceeding the optical range of vision this system will offer a reliable 24-hr communication service, free from fading, interference with other stations, static interference, and risk of overhearing. As a result of the bending of the rays, the optical range of sight may even be greatly exceeded, and from practical results, a satisfactory communication service has even been established when optical visibility was not obtainable, *e.g.*, with intervening hills, etc.

For ultra-short-wave (VHF) systems the aerials are very simple in construction and require comparatively little space. The simplest form of aerial is a half-wave dipole, erected either vertically or horizontally.

From the equipment point of view the VHF transmitter and receiver are comparatively of a very reduced size and very simple in design and operation. They can be maintained and operated by non-technical operators. If required, provision can also be made for automatic calling and for extension facilities to normal telephone physical circuits.

Communications for Geological and Geophysical Parties

There is little doubt that for mobile geological and geophysical exploration parties radio offers an ideal medium for meeting the requirements of rapid and flexible communication. In general these parties are called upon to operate in undeveloped regions, frequently in localities entirely remote from civilization, and so precluding the use of any means of communication other than wireless. The main requirements of this type of service are

(*a*) between mobile survey vehicles and surveyor's camp, and
(*b*) between the surveyor's camp and distant base.

Survey parties are mobile to a high degree. For this reason every consideration must be given to minimizing the weight and bulk of equipment. The equipment must be of robust construction to withstand shocks and vibrations, as the apparatus may be installed in motor-transport vehicles intended for use over rough and undeveloped country. The components must be easily accessible for easy installation and operation, by non-professional personnel if necessary.

Difficulties in obtaining satisfactory power supply should be borne in mind when arranging this type of service. As far as possible the whole mobile equipment should be made to operate economically from available 6- or 12-volt car batteries, with HT provided by either vibrators or rotary convertor units. Transmitter-power output to aerial in the region of 8 to 10 watts is a satisfactory figure at the frequency suitable for local mobile work of this type, *i.e.*, between 1·5 and 3 mc. The load drawn from the battery source will then be around 100 watts, and this figure will determine the ampere-hours of the battery to be used.

Using a 15- to 20-ft whip aerial a radio-telephony range up to 20 miles can be expected over an average terrain with that power. This range can be extended quite considerably where it is possible to set up a larger aerial.

At camp sites one or two more powerful sets may be carried. A portable installation of 20 watts transmitter power to aerial is reasonable, and the set should provide a frequency coverage from 1·5 to 15 mc/sec to permit communication with the supply base which may be as much as 300 miles distant. Here too, it is advisable to provide battery operation also, as other camp supplies are not to be considered entirely reliable. In certain cases where the normal modern means of transportation are not available, it may be necessary to provide equipment in the form of mule or camel pack-sets with pedal-generators for the source of power.

The installation being of a semi-permanent nature, dipole aerials may be erected to advantage on the channels to supply base; for purely local transmission to survey vehicles in the field a single-wire T aerial is probably best suited, and this can be obtained by connecting the HF dipole aerial-feeder wires together.

The service requirements will normally be satisfied by simplex method of operation, *i.e.*, one frequency for sending and receiving, using one aerial with a manual change-over switch from sending to receiving. The services from surveyor's camp to distant base should also include facilities for telegraph service. To avoid continuous watches the usual practice on this type of service is for the stations to establish communication at predetermined

fixed times. This also would apply to a mobile station in contact with its base on a permanent wireless watch. Another essential requirement is reception of accurate time signals by wireless for checking chronometers used by survey parties operating in remote localities where accurate maps are not available.

In certain areas where the terrain to be covered is known to be flat, or with few intervening high hills, VHF equipment (30 to 300 mc), due to its propagation properties, may offer quite a good solution for mobile service. Its main advantages are reduced size of equipment and aerials, small power, reliable and good quality communication, and absence of fading and interference.

Either amplitude-modulated or frequency-modulated systems can be used for VHF communication. The latter has the advantage of better signal-to-noise ratio and a very stable signal strength. For a given transmitter output the FM system will operate over a greater distance than the AM system. The output of a transmitter will depend on the range to be covered, although ranges between vehicles should not be expected in excess of 10 to 15 miles, and the 5-watt system will cover satisfactorily this range. If aerials can be raised to a more effective height, say 80 ft, ranges up to 30 miles may be covered satisfactorily.

As can be seen from above no definite general solution can be given as each case will require individual consideration of the factors involved in the problem, and each requirement will need an individual solution.

Land-line Communication.

General Considerations.

For the benefit of those not connected with this particular branch two diagrams are reproduced from a previous paper published by the author ("The Propagation of Electromagnetic Waves on Long-distance Telephone Lines," *Distribution of Electricity*, January 1934, page 1422) which will enable the forming of a physical conception of the process that electromagnetic waves undergo when transmitted over a pair of wires from an emitting point A to a more or less remote receiving point B. Fig. 2 shows the transformation that human speech undergoes during its transmission and the different phenomena which affect its quality, and Fig. 3 indicates the principal factors which control the propagation and also shows how these factors affect the transmission. Both diagrams are self-explanatory.

Landline communication can be accomplished by either of the following methods :—

(*a*) Long-distance lines : by open-wire lines with or without repeaters, by cables with repeaters or, where several long-distance lines are required over the same route, by unit-channel carrier systems, superimposed on physical lines (open-wire lines or underground cables).

(*b*) Subscriber lines and short junctions or tie-lines : by open-wire lines, by aerial or underground cables, or by a combination of the two or three methods.

It is hardly possible to make any theoretical comparisons which of the above alternative methods would provide the best solution, as such study

would be of little practical value in view of the great number of variable factors and local conditions involved in each case. Nevertheless, a private telephone system is usually engineered to cater for a known demand, and no difficulties should be experienced in making comparative studies of the various possible solutions from economical and technical points of view.

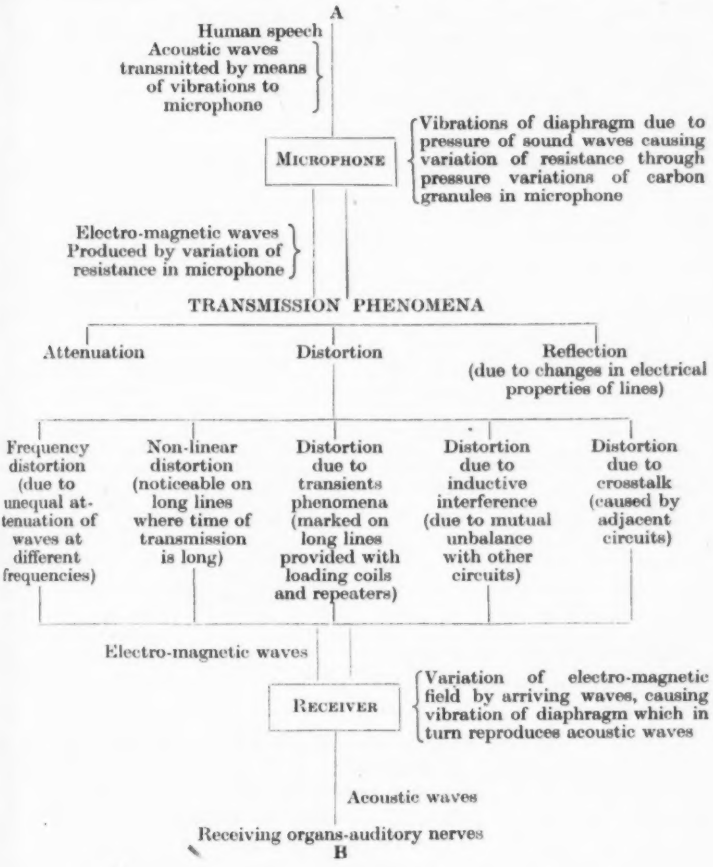
A
Human speech
Acoustic waves transmitted by means of vibrations to microphone
MICROPHONE
Vibrations of diaphragm due to pressure of sound waves causing variation of resistance through pressure variations of carbon granules in microphone
Electro-magnetic waves Produced by variation of resistance in microphone
TRANSMISSION PHENOMENA
Attenuation
Distortion
Reflection (due to changes in electrical properties of lines)
Frequency distortion (due to unequal attenuation of waves at different frequencies)
Non-linear distortion (noticeable on long lines where time of transmission is long)
Distortion due to transients phenomena (marked on long lines provided with loading coils and repeaters)
Distortion due to inductive interference (due to mutual unbalance with other circuits)
Distortion due to crosstalk (caused by adjacent circuits)
Electro-magnetic waves
RECEIVER
Variation of electro-magnetic field by arriving waves, causing vibration of diaphragm which in turn reproduces acoustic waves
Acoustic waves
Receiving organs-auditory nerves
B

FIG. 2.

THE TRANSFORMATION PROCESS OF ACOUSTIC WAVES INTO ELECTRO-MAGNETIC WAVES AND VICE-VERSA IN A TELEPHONE CIRCUIT.

For a summary comparison, however, it is possible to formulate the following general rules : cable circuits are less vulnerable to damage than open-wire lines, but though more reliable, the probable need for easy accessibility from any point of the line renders communication by cables in certain cases impracticable. This is particularly true during construction of distant

pipelines or large refinery areas where the existence of easily accessible telephone lines, built ahead, largely contributes to the saving of time, labour, and costly errands. However, for normal operation in centres requiring extensive telephone networks, such as oilfields and main loading or pumping stations, it may be found more expedient to run a cable to a central distribution point and extend individual circuits by open-wire lines. This method will also contribute to a certain saving in the cost of construction as the cost of ducts and labour will practically remain the same for any size of cable. It is always advisable when laying a cable to provide a reasonably liberal reserve of spare pairs for any possible future extensions.

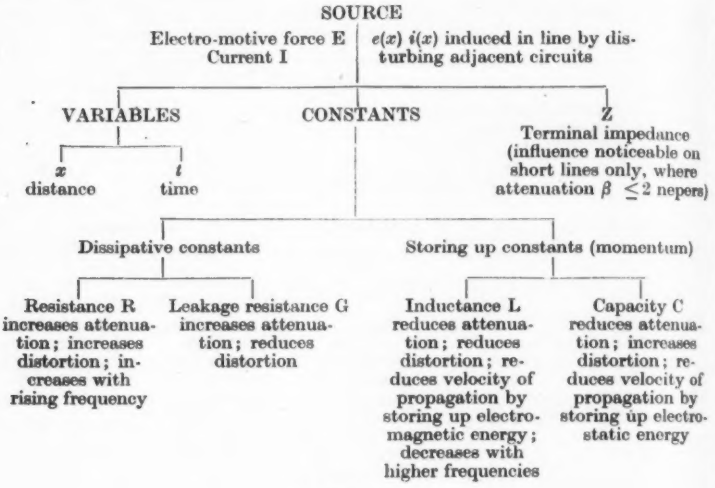
SOURCE
Electro-motive force E
Current I
e(x) i(x) induced in line by disturbing adjacent circuits
VARIABLES
CONSTANTS
Z
Terminal impedance (influence noticeable on short lines only, where attenuation β ≤ 2 nepers)
x
distance
t
time
Dissipative constants
Storing up constants (momentum)
Resistance R increases attenuation; increases distortion; increases with rising frequency
Leakage resistance G increases attenuation; reduces distortion
Inductance L reduces attenuation; reduces distortion; reduces velocity of propagation by storing up electromagnetic energy; decreases with higher frequencies
Capacity C reduces attenuation; increases distortion; reduces velocity of propagation by storing up electrostatic energy

FIG. 3.

ELECTRICAL PROPERTIES OF LINES AND THEIR INFLUENCE ON PROPAGATION OF ELECTRO-MAGNETIC WAVES.

Trunk Lines.

In view of the very small number of trunk lines normally required for telephone and telegraph service on private systems, the cable solution will always prove very costly and impracticable. On the other hand, a possible criticism of policy of ensuring so important communication channels by open-wire lines may be compromised to some extent by the fact that, as in the case of pipelines, the lines will constantly be patrolled by linesmen whose conjoint duties will also be to patrol the pipeline which will run alongside the telephone route, provided such a construction is possible.

Furthermore, the opinion that cables offer a better solution to an efficient long-distance communication service needs a serious revision. In the early stage of development of telephony, and before the advent of telephone repeaters and carrier telephony, it was found necessary to change over from the primitively built open-wire lines to underground cables. However, as

open wires can transmit wider frequency bands and possess better transmission qualities, they may be turned, with the present improved line-construction practice, to a more profitable use by superimposing over one pair one or more additional carrier channels.

Open-wire Lines.

Theoretically, it is impossible to expound a general rule which type of wires and poles will provide the best service and the most economical design. However, it may not be out of place to discuss briefly the relative merits, *per se*, of the different conventional methods of construction.

Wooden poles are the most common form of supports for telephone and telegraph lines. They have a large torsional strength and a considerable elasticity. However, their usefulness is very limited as they do not resist fire. Their other objectional features are : their cost of transportation, which is comparatively high on account of their weight, and the fact that in certain localities they may deteriorate rather rapidly. Steel poles, on the other hand, can be more easily conveyed as they are manufactured in convenient lengths and weight and their life is indefinitely long if properly protected.

It is always advisable to keep the line as low as possible as the stresses on poles increase with their height. A convenient average clearance of wires from ground is 16 to 18 ft. This clearance is usually higher for road, river, railway, and electric-line crossings. The heights of these clearances are governed by local conditions and regulations.

The pole spacing, or span length, will depend on the size of the wires, their separation, and permissible sags. With few wires on the poles the span lengths may be increased above the standard length. The average standard span lengths vary between 50 and 75 yards. For the purpose of obtaining the greatest benefit from the transposition of the wires, especially where the introduction of carrier telephony is envisaged, these spans must remain as uniform as possible for the whole length of the line. The proper separation of wires for these spans is 8 to 12 in and that of pairs either equal to the latter or increased to 12 to 18 in.

On a properly constructed open-wire telephone route, regularly patrolled and subjected to periodical preventive maintenance work, the number of line faults from natural causes is comparatively quite small. Table III, extracted from a statistical investigation carried out by the writer on five different long-distance trunk lines, shows the number of faults encountered over a period of six years.

TABLE III.

Line.	Type of wire, lb/mile Cd–Co.	Length of line examined, miles.	Period, years.	Average number of faults per mile per year.
1	300	250	6	0·125
2	300	250	6	0·117
3	200	250	6	0·121
4	200	250	4	0·135
5	70	40	6	0·685

The first four lines form part of a 600-mile trunk circuit. The percentage loss of working time per calendar month, calculated on a 24-hr basic period of interruption, due to these faults was found to be as follows, the faults being cleared only during daylight :—

Line.	Loss in percentage.
1	2·99
2	2·02
3	2·38
4	2·72
5	2·28

These losses compare very favourably with the standard limits of the British Post Office.

The qualities required in telephone and telegraph wires are mechanical strength and ability to resist corrosion. There are various types of wires available on the market claiming different advantages. The most commonly used is copper wire which is fairly immune from corrosion and has a high tensile strength. Cadmium–copper (Cd–Cu) wire is to be preferred to hard-drawn wire as it has a higher breaking strength, though its electric resistance is slightly higher. The size of wire to be chosen will depend on transmission requirements, and as oil companies need not respect international regulations, in so far as transmission quality is concerned, it is sufficient to aim at an overall loss of 12 to 15 db for a good commercial speech. However, as already alluded to, it is essential that consideration be also given to mechanical strength of the wire to ensure a reasonable safety to the line.

The C.C.I.F. (Comité Consultatif International for Telephony) does not recommend the construction of long-distance open-wire lines with wires of less than 3 mm in diameter (approximately 300 lb/mile) as the modulus (absolute value) of an open-wire line of 3 mm or heavier conductor does not vary by more than ± 5 per cent within a temperature range of from $+45°$ C to $-25°$ C. On the other hand, very long circuits of smaller-diameter wires (2·5 mm) may show variation of the impedance which may be sufficient to necessitate adjustments of the repeater gain or balancing networks.

For short circuits such as local junctions between switchboards, lines to outlying distant water wells, etc, up to a distance of 100 miles, smaller-gauge wires of the 70 lb/mile or 100 lb/mile type may be used. These gauges amply satisfy the transmission requirements for the above range and they are also used for the same purpose by postal administrations on public-telephone systems. However, when comparing faults and working-time losses on lines of different gauges, running over the same pole-route and length, the writer has found that the initial saving obtained from the reduced cost of the smaller-gauge wire is outweighed by the increased cost of labour incurred in clearing the far greater number of faults on the smaller-gauge lines.

Comparing the additional cost of labour and transport expenses with the difference in cost between the wire gauges it has been found that the additional cost of the heavier gauge wire could have been compensated for in

approximately twelve years. This calculation did not include the loss in revenue caused by the line being thrown out of commission, which, on a private system, could only be given a hypothetical value, but would be a factor of paramount importance on public lines. Moreover, the useful life-period of the line was not considered. Practical experience has shown that the 70 lb/mile line exhibits definite signs of deterioration in strength, due to ageing after a period of ten to fifteen years, whereas heavier-gauge lines, operating under identical climatic conditions, appear to be still completely free from this effect after the same period. It would therefore appear that the 200 to 300 lb/mile wire gauges offer a more economical solution for the above type of lines.

Transmission Requirements.

On modern public-telephone circuits transmission losses are mostly confined to local lines, junctions, exchange equipment, and local party's installation losses. The trunk lines, on the other hand, are now designed to operate at a very low loss, and sometimes even at zero loss, the actual line attenuation loss being compensated by the gain of the amplifying apparatus. Private communication systems, however, with their predetermined and limited range of operation, need not necessarily follow these rules, and from the writer's experience the following approximate distribution of losses will meet all the practical requirements for a good communication circuit on an oil company's private-telephone system :—

(*a*) local lines : up to 5 db;
(*b*) trunk lines : up to 10 db;
(*c*) exchange losses : up to 4 db.

Traffic Requirements.

(a) *Local Lines :* On private-telephone systems it is quite easy to determine line requirements in advance, as these will largely depend on known exchange capacities and spheres of activities. Generally, it will be found that on oil companies' private-telephone systems, two to four junctions will in most cases meet all the requirements for a satisfactory inter-exchange flow of telephone and telegraph traffic.

(b) *Long-distance Trunk Lines :* With the present modern means of communication, two trunk lines will practically meet all possible requirements for long-distance traffic between oilfields and a terminal loading centre interconnected by a pipeline. Namely, one as a direct line between the two terminals, and the other as an inter-station line passing through all intermediate pumping stations. This capacity will, in most cases, prove quite sufficient for normal requirements. However, should the traffic increase to such an extent as to necessitate the provision of additional communication channels, the superposition of one or a multi-channel carrier telephone equipment offers the best and cheapest solution. It may then be found expedient to re-arrange the circuits in the following manner ; one physical line to carry the traffic between the intermediate and terminal stations, and the superimposed carrier on the same line to ensure communication between the two terminals. The other physical line may then act as a spare line between the stations for rapid substitution of faulty sections

pending the clearance of faults, or as an additional telephone and telegraph channel.

Nowadays, one physical open-wire pair on a properly constructed and transposed pole-route of any length can carry the following standard equipment :—

Telephone Channels.

Voice frequency . . .	1 channel.
Single channel carrier . .	1 „
Three „ „ . .	3 channels.
Twelve „ „ . .	12 „
	17 channels.

Telegraph Channels.

Up to	18 channels and more if necessary by using one or more of the speech channels.

Equipment.

Having determined the number of operating channels, the next question to be solved is the method of operation. In large companies there are two distinct phases of operation, and communication requirements during these two phases are very diverse in character. During the first phase, that of construction, the traffic distribution is very high and irregular. The equipment is moved from one place to another, and not infrequently housed in temporary buildings where it must be installed and brought into operation in the shortest possible time. It is therefore essential that during this period very simple equipment, robust in construction and easy in operation, be used. For telephony, the simplest equipment is local-battery- (LB) operated switchboards and instruments with a magneto-ringing system for signalling.

Where the LB-telephone system is employed cord-circuit switchboards should always be preferred to the cordless type switchboards, irrespective of the switchboard capacity. From experience gained with the latter type of switchboards, the writer has found that the keys utilized on that type for the purpose of switching through the lines, frequently develop high transmission losses, due to high contact resistance, caused by either dust accumulation between contacts, wear, or deterioration of the keys' spring elasticity.

Where it is considered that a satisfactory maintenance service and frequent replacement of batteries will constitute a difficult problem, the common-battery (CB) system of operation will provide a satisfactory alternative solution. On this system, the switchboard and subscriber instruments are fed from a common or central battery of the secondary type, which is maintained and periodically re-charged at the point where the switchboard is installed. However, even with this system, very distant subscribers, such as outlying wells, tanks, etc, will have to remain on local-battery positions on the CB switchboard, otherwise the feeding current supplied from the distant switchboard would be too weak for a satisfactory operation of these telephones.

Telephone Instruments.

Subscriber telephone instruments may be either of the stationary type, table or well type, or portable telephones which can be connected to, and at,

any point of the line with the aid of contact rods. Where both types of telephone systems are used, it is sometimes found desirable to adopt universal type instruments, suitable for both systems, thus considerably simplifying maintenance service and the spare-parts problem. Portable telephones are usually constructed on principles entirely different from those of stationary types. They must be robust in construction, to withstand rough and open-air handling, and should be light in weight and as little bulky as possible. There are at present instruments of this type not exceeding 9 lb in weight.

For tank-farms, on tankers, or in any fire-sensitive atmospheres special fire-proof mining-type telephones are employed. In this type the places where sparking is liable to occur are so enclosed that any flame which may result from the ignition of the enclosed gas mixture either cannot pass to the outside atmosphere or is cooled in its passage to render it completely harmless to the most inflammable atmosphere.

For permanent operation the choice may fall back on the manual operation used during the construction period or on automatic telephony. Automatic operation is superior to manual when the number of subscribers is large.

Line Signalling.

Where several instruments are required to be left permanently connected across the same line, the following points must be observed to ensure a satisfactory reception of the signalling current on all telephones : (*a*) the ringing generator of each telephone must have powerful magnets (cobalt steel) to ensure a high output; (*b*) the bells must be of the high-impedance type, sufficiently sensitive to operate with weak currents; and (*c*) to prevent an appreciable decrease of the signalling current, should any of the telephones' speech circuit be left open, a condenser of approximately 1 microfarad is to be inserted in the speech circuit. The presence of this condenser increases appreciably the speech-circuit impedance at ringing current frequencies.

Where several stations have to be operated in tandem on the same line, selective calling is sometimes resorted to. With this system each station can be called individually, and this can be realized by the following different methods :—

(*a*) Code signalling;
(*b*) Selective ringing over both wires and wire to earth;
(*c*) Impulse ringing by means of rectified ringing current in only one direction;
(*d*) Delayed action ringing relays;
(*e*) Automatic selective calling, by either sub-audio or audio frequencies.

Telephone Repeaters.

Excessive transmission losses on long lines are compensated by specially designed two-way amplifiers known as telephone repeaters. These repeaters are usually inserted in the centre of the lines or at regular intervals.

Telephone repeaters will not pass efficiently the low frequency (17 to 100 cp) ringing currents. These have to be by-passed by simple low-pass

filters or regenerated at the repeater points. Alternatively, they can be modulated with a speech frequency and transmitted through the repeaters and then demodulated at the receiving end.

In certain cases it is found more convenient to locate the repeater at the end of the line. This type of repeater, known as cord-circuit repeater, is terminated on the switchboard and controlled by the switchboard operator.

Repeaters operating on private telephone systems, though generally following the conventional design, need not strictly adhere to all the standard performance requirements, recommended by the C.C.I.F. for public and international circuits. Their circuit may consequently be considerably simplified to facilitate its maintenance by semi-skilled or non-technical personnel.

Carrier Telephony.

As has already been mentioned, the capacity of a telephone circuit can be increased by the superposition over the physical pair of a number of carrier telephone channels. The capacity increase obtained by this method offers the best and most economical solution.

The fundamental principles of carrier telephony, now so widely used, are based on a frequency transformation of the transmitted speech from its voice-frequency range to a higher band of frequencies during the transmission from one terminal to the other. This is realized by means of amplitude modulation of the speech frequencies with a higher carrier frequency produced by a carrier oscillator. At the receiving end the complex wave is demodulated and the unnecessary frequencies suppressed with the aid of selective circuits known as filters. Theoretically, a physical pair can carry any number of carrier channels, and certain circuits are now being designed, in conjunction with modern co-axial cables, where as many as 240 simultaneous telephone conversations can be passed over a single pair of conductors (" A Million Cycle Telephone System " by Strieby, *Bell System Technical Journal*, January 1937, page 1). The company with which the writer is connected operates on its private system single-channel and three-channel carriers, one providing a direct telephone channel between two stations over a distance of 630 miles. These carriers are being augmented in the near future by further three-channel and twelve-channel carriers.

A single-channel carrier system, particularly useful for oil companies because of its simplicity, is the type having one passive end. This comparatively simple and cheap system will provide an additional telephone channel when superimposed over a pair of conductors over a distance of approximately 10 miles. The particularly advantageous feature of this system is that one end of the equipment is completely passive and may therefore be installed in a distant station lacking completely in qualified staff.

The novelty and advantages of the system are as follows :—

(*a*) One end is completely passive, *i.e.*, there are no valves or any moving parts requiring replacements, and no power is required with the exception of a 3- to 6-volt battery for an alarm bell. The passive end, therefore, may be located in places lacking completely in technical staff and power-supply facilities.

(*b*) The system, being portable, may be connected to any line between a station and a distant temporary camp, thus providing an additional speech channel within twenty to thirty minutes.

(*c*) The conversations on the carrier channel cannot be listened-in to on the line, the speech being scrambled between the two terminals.

Telegraphy.

For telegraphy during temporary construction periods, the simplex earth-return telegraph system superimposed on both wires of a telephone circuit, offers the most convenient method of operation. Thus, in case of a contact between the two wires or breakdown of one of the wires, the telegraph remains in operation over one wire and earth and maintains the telegraph service.

This method provides telegraph transmission of only one message at a time by Morse Code by manually operated keys or by teleprinters, which can be operated by any non-skilled person knowing how to use a commercial typewriter.

For permanent operation either the simplex telegraph system may be retained or telegraph typewriters (teleprinters) introduced. During the last few years there has been a growing recognition of this new type of telegraph transmission, which is steadily replacing the Morse key and sounder operation. This system is of particular interest to oil companies because it employs a transmitting method based upon commercial-typewriter principles and therefore does not necessitate the employment of special Morse-Code operators. The system also enables messages to be received automatically, and therefore dispenses with the need for constant attendance of an operator. However, in oil companies, this feature is not very desirable, as certain telegraphic messages may require immediate attention and therefore the necessity for constant attendance is to be preferred. The speed of operation of teleprinters can reach seventy words per minute against thirty to thirty-six words per minute on the manually operated simplex sets.

Telegraph Fork-Repeaters.

On long telegraph circuits, consisting of two sections, with several telegraph circuits operating in series on each section, the current strength, due to line leakage and other losses, may not be strong enough to operate satisfactorily distant telegraph relays, and the telegraph signals must therefore be repeated or reproduced at an appropriate point of the line. This is realized with the aid of a telegraph repeater, usually situated at the end of a section, which automatically reproduces and transmits the signals to the other section. On telegraph circuits consisting of several sections fork-repeaters are used, usually located at the bifurcation point.

A telegraph fork-repeater will automatically re-transmit telegraph signals from any of the terminals to the bifurcation point and to the other terminals, or from the bifurcation point to all terminals or to any particular terminal(s). A transfer set associated with the repeater will also provide facilities for independent and simultaneous operation between the bifurcation point and one of the terminal stations on the transfer set and between the remaining terminal stations through the fork-repeater.

The number of telegraph channels can be increased by either providing separate multichannel voice frequency and/or high-frequency telegraph equipment, or by S + DX sets which allow one extra two-way telegraph channel for each speech channel.

Oil Despatchers' Communication Service.

General Scope.

The oil-movement control carried out by the oil despatchers constitutes one of the most important activities of an oil company. It follows that an effective supervision by the oil despatchers is of the greatest importance.

The oil despatcher's duties are to supervise the pumping operations. To carry out effective supervision he must be able to send his instructions and to receive pumping-operations details with the least delay.

The bulk of the oil despatchers' traffic is formed by the regular arrival of oil figures (quantities pumped through, tank gauging data, speed, etc) from all pump stations on the pipeline at fixed times.

In addition to the above he must have direct access to any of the stations' shift engineers on duty immediately anything occurs, *e.g.*, engine troubles, alterations in pumping programmes, delays, defects; briefly, anything that may affect the regular flow of oil.

The oil despatcher may also want to put into operation a collective call to a number of stations or a general call to all stations.

Furthermore, in addition to the regular oil-pumping data and the traffic emanating from the oil despatcher, the shift engineer on duty at a pump-station may want to advise the oil despatcher of unusual happenings at his end.

Type of Service.

The shift engineer must be able to transact his business from his desk in the pump-house where normal transmission and reception of speech is impossible owing to the excessive noise produced by running engines. From these considerations it is evident that the most desirable form of communication system, satisfying the specific needs of this service, is best met by a reliable record-form-type teleprinter telegraph service. With this system the figures and messages are received in printed form thus avoiding any possible errors from wrong verbal reception, and the transmission and reception of messages is not affected by the pump-house noises.

Other considerations leading to the adoption of this type of communication service are : simplicity and reliability of equipment; easy servicing; simplified transmission requirements; and cost. Moreover, it would be impracticable and expensive to provide this type of service with speech channels.

Justification for an independent Oil Despatchers' Communications Service.

On a general communications system of an oil company the oil despatcher has to meet strong competition from other equally important traffic from other departments.

The ability of the oil despatcher to clear his own traffic eliminates the

passing of his requirements to the telephone or telegraph operators and the unavoidable delay caused by engaged lines and other priority requests.

As the response of the machines on the oil despatcher's system is normally immediate the saving of time is considerable—a very important factor in oil-pumping operations.

The possibility of an error in transmitting oil figures is transferred from the human element to the machine. Furthermore, the system also eliminates altogether the intervention of telegraph operators in the process of oil figures' transmission between the shift engineer and the oil despatcher.

By the removal of this traffic from the general-communications system a marked improvement is obtained in the general-communications service of the company since the circuits are free to handle other traffic.

The Iraq Petroleum Company's Oil Despatchers' Communication Service.

The following is a brief description of the system developed by the writer in conjunction with engineers of Standard Telephones and Cables Ltd., London, and now being manufactured by the latter for use on the I.P.C. pipeline system.

This system will offer the oil despatcher facilities for direct communication, without the intervention of any operators, with the shift engineers on duty at any of the pump-stations and vice versa, or with a number of stations or all stations simultaneously, by a simple operation of the appropriate keys on his desk.

The system will be superimposed on open-wire lines without depriving these lines of any of their existing telephone and telegraph channels. It will also not interfere with the possible future addition of a twelve-channel carrier system, and simultaneous transmission will take place, over the same pair of wires, of the company's general telephone and telegraph traffic and the oil despatcher's own traffic, under his direct control.

The system is realized by the application and adaptation of known principles and methods and, to a great extent, it constitutes an application of the knowledge and experience already gained in carrier transmission, voice-frequency telegraphy, automatic telephony, and long-distance dialling, and is built up of standard and approved telephone and telegraph parts for both electronic and switching components. These individual devices have all proved their reliability and safety in actual practice.

Brief Description of the System.

The equipment consists of a modified high-frequency telegraph system and a selective signalling system.

The oil despatcher controls from his central location three pipelines, one with two terminals, one intermediate and one subsidiary intermediate station situated near one terminal, a second with two terminals and five intermediate stations and a third pipeline with two terminals and four intermediate stations. The approximate length of each pipeline is as follows : the first—150 miles, the second—470 miles, and the third—380 miles. The open-wire line on each section consists of a pair of 300 lb/mile cadmium–copper conductors.

For transmission purposes the three line sections have been considered separately and each is complete in itself.

On the transmission side one frequency is allocated to each station on a branch line for transmission towards the central oil despatcher's station where all are converted to a common frequency transmitted back to the called station for selecting and teleprinting.

The scheme gives a normal condition of tone on line which is necessary for the proper working of the automatic volume control in the detectors.

Selective Calling.

The system provides selective calling between all the intermediate stations and the terminals on each line. The oil despatcher is provided with a set of buttons for the selection whereas the other terminals and the intermediate stations are provided with a dial for the selection.

The selective circuit consists of telephone-type relays and calls are set up by dialling a single digit. One digit is reserved for group calling and one for broadcast messages. The selective circuit consists of a relay counting train and arrangements are made so that by strapping on a terminal strip any number can be allocated for any required function.

The selective circuit is operated by the same relay which actuates the teleprinter.

Facilities.

1. The oil despatcher is able to call any station and vice versa.
2. Each station is able to call any other station on the same branch line and via the control station any station on another branch.
3. The oil despatcher is able to call two or more selected stations of one branch line and send a " broadcast " message to these stations.
4. When any call is in progress a busy indication is given at the station not taking part.
5. When a call is in progress any other station is able to monitor and to break in and clear down the connexion if a more important message is to be sent.
6. The controller is able to broadcast to stations on more than one branch line.
7. In case of a breakdown of a line the system can be easily switched over to another pair of wires on the same route.

Signalling. Remote Control.

Another important feature forming part of a modern communications system of an oil company is remote signalling. Remote signalling finds a very wide field of application in refineries, pump-houses, loading stations, etc. It is used to control from a central station the diversified activities of these points such as the operation of various units and tanks and for the remote loading control of tankers. The requirements are numerous and very diverse in character and in each case the design is based on the actual service requirements.

Maintenance.

Even the best-designed equipment is of little use if it is not properly maintained, and a systematic preventive maintenance will find its full compensation in a satisfactory operation of the equipment.

Open-Wire Lines.

The conditions of the lines must be verified each morning. When the test shows the existence of a fault, immediate steps must be taken for its rapid removal as, particularly in oil companies due to the restricted number of alternative circuits and the important nature of the transacted traffic, a speedy restoration of faulty lines is a matter of great importance. It is essential that the distance to be patrolled by the linesmen shall be such that it can be covered in not more than one day. This requirement will also indirectly determine the locations of the linesmen, whether motor transport, mounted or foot linesmen. On long routes, carrying important circuits, shorter patrol sections should be provided, and if necessary, the patrol and fault-clearance service extended to full 24 hr. In the latter case the night patrol can be carried out with vehicles provided with strong spotlights mounted on specially provided adjustable pivots.

To facilitate testing and fault localization open-wire lines must be provided with specially designed test insulators with removable links. The distance between these test points shall not exceed 50 miles. A particularly useful type of test insulator is the type known as vacuum-fuse insulator which, in addition to being a test insulator, also affords protection against induced currents and voltages caused by lightning discharges and statics. With this type of insulator the splitting of the line is carried out by the removal of a screwed cap which breaks the continuity of the line. This method ensures better protection against possible loose contacts, frequently present with the ordinary type test insulators.

Special care must be taken to instil in the linesmen the idea of preventive maintenance based upon the idea of systematic and complete inspection of small sections of the line, when not engaged on actual fault-clearing patrols.

Cables.

Cables do not require the same amount of maintenance as overhead lines. Regular conductivity and insulation tests are, however, necessary, and any drop in insulation immediately investigated and if necessary the cable desiccated. The latest method of desiccating cables is by applying silica gel. This is a very hard vitreous substance and its chemical composition is SiO_2. It is specially prepared so that its structure will absorb moisture to the extent of 40 per cent of its own weight without increasing in volume. It may subsequently be heated and restored to normal conditions and re-used. This method of desiccating has now practically superseded the old methods of drying-up cables. Silica gel can also be placed inside switch-boards, wireless apparatus, and other equipment situated in damp places. Where larger equipment is involved, such as complete automatic exchanges in localities with excessive humidity, continuously running silica gel plants can be installed. Another possible source of harm to cables is corrosion from stray currents or caused by chemical action. Its effect can be mitigated by restricting the amount of stray currents, by taking care that the cable is clear of water and by making liberal use of petroleum jelly when drawing the cable and by a reliable electrical bonding of the cable sheathing.

Apparatus.

An equally important matter is the maintenance of the apparatus, and a comprehensive and systematic maintenance routine must be instituted which will ensure that all apparatus is maintained in an efficient way. All instruments must be periodically examined for loose contacts and faulty parts, moving components lubricated, contacts cleaned, and burnt ones speedily replaced. Batteries must be periodically checked, and manufacturers' instructions strictly adhered to.

It will also be found very convenient to maintain an instrument-repair shop for the repair of instruments and manufacture of small parts, etc.

A conscientious performance of these maintenance duties will find its full reward in a smooth and satisfactory operation of the system.

Organization.

No paper of this nature could be complete without some reference to organization of a telecommunication department in an oil company.

In public telephone and telegraph administrations it is customary to separate the traffic from engineering because of dealings with the public. In oil companies it is generally preferred to co-ordinate both services under one organization. The right approach to the problem of organizing a communications department is to base its constitution and functions on the importance of the service, nature of equipment installed, and amount of traffic to be handled. In a large concern with a considerable communications system a correct and rational organization of the service is of vital importance. There, an independent staff will ensure the maintenance of the equipment and assume full control of the traffic and its distribution. In certain cases it will take also a share in the oil-movement control and gauging duties.

In companies where the equipment and amount of traffic do not justify maintenance of a separate communications organization these duties may be carried out by the electrical engineer, electricians, oil gaugers, etc.

Acknowledgements.

The author's thanks are due to the Iraq Petroleum Co. Ltd. for permission to publish this paper.

The author would also like to acknowledge the helpful criticism of J. E. F. Walsha of the section dealing with radio communication in general and for his assistance in preparing the section on radio communication for geological and geophysical parties.

AN ACCURATE MICROVISCOMETER.

By Erica Glynn and L. Grunberg.

The rate of flow of a liquid from a reservoir under a constant applied pressure into an empty capillary was first used by Bingham and Murray [1] for the measurement of viscosity. The method to be described here is based on the same principle and is applicable to very small quantities of liquid. The diameter of the capillary is chosen with regard to the viscosity of the liquid and the quantity available. For viscosities lying between 1 and 100 poise, a capillary of radius 0·01 cm gave fifteen accurate values of the viscosity at any chosen temperature, 10 to 15 mg of material being sufficient. For liquids of higher viscosity (100 to 1000 poise), larger capillaries (radius up to 0·03 cm) were used with a corresponding increase in the weight of material required (40 to 80 mg). The accuracy obtainable is of the order of 0·5 per cent.

Since the rate of flow of liquid decreases continually as the capillary fills, the pressure being kept constant, thixotropic or "anomalous" behaviour is readily detected. The method is particularly suitable for opaque liquids, since it is the rate of filling of the capillary which is observed.

Apparatus.

The viscometer (Fig. 1) consists essentially of a piece of capillary tubing T (diameter 0·01 to 0·03 cm, length 20 cm), bent at right angles at one end

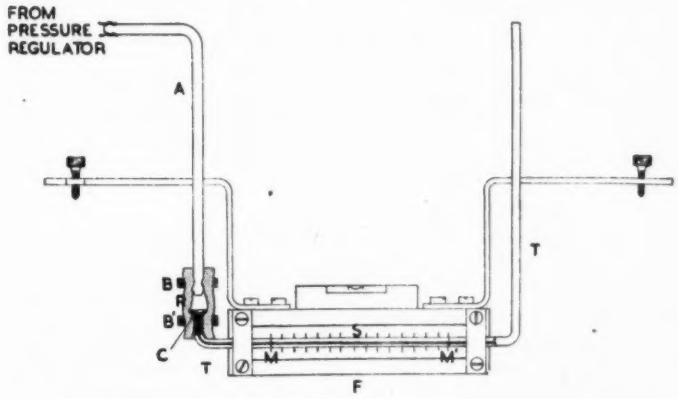

Fig. 1.

which is shaped into a small cup C. A wider capillary T', also bent at right angles, is fused to the other end of T. The tube T carries two marks M, M', 15 cm apart. The cup C is connected to the glass tube A by means

of the rubber sleeve R. Two circular metal clamps B and B' ensure the tightness of the joint. The whole is clamped securely into a frame F against a mirror scale S, so that the mark M corresponds to the zero of the scale S. A spirit level on F ensures that the viscometer may be kept horizontal by suitable adjustment. It is immersed in a thermostatic bath with clear transparent walls, kept constant within $\pm$ 0·02° C. The thermometer is graduated in 0·1° C per mm of scale.

A constant excess pressure of air is applied by means of a pressure regulator as used by Stone [3] (Fig. 2). Two similar cylindrical bulbs are

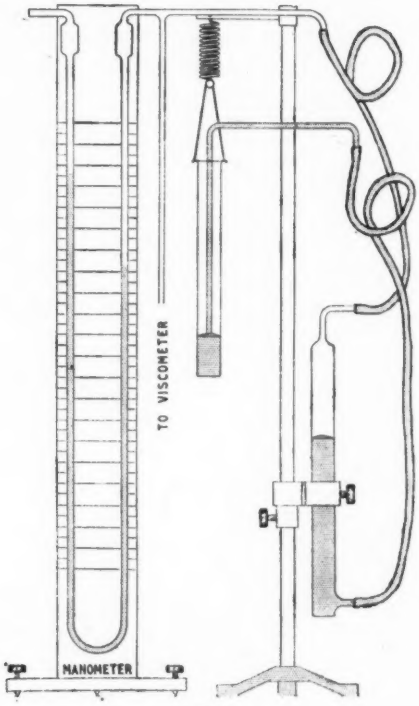

FIG. 2.

connected by a syphon and rubber tubing and contain mercury. The lower bulb is fixed in position and the upper bulb suspended freely from a spring. This system gives very constant pressures if the extensibility of the spring is such that when a volume of mercury Ax (A = area of cross-section of each bulb) flowed from the upper to the lower bulb the spring contracted in length by an amount equal to $2x$. Both positive and negative pressures may be obtained with this system by suitably adjusting the volume of mercury in each bulb at atmospheric pressure. The pressure is measured on a mercury manometer.

The viscosity of a liquid flowing into such a viscometer is given by (Barr [2])

$$\eta = \frac{PR^2t}{4(l^2 - l_0^2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where η = viscosity,
R = radius of capillary,
P = pressure,
l = total length,
l_0 = length to first mark on scale,
t = time in seconds to flow from l_0 to l.

From (1)

$$\frac{(l - l_0)}{t} = \frac{R^2P}{4\eta(l + l_0)}.$$

Let $s = l - l_0$ = scale division reached in time t, then

$$\frac{s}{t} = \frac{R^2P}{4\eta(s + 2l_0)}$$

and

$$\frac{t}{s} \cdot \frac{P}{\eta} = \frac{4}{R^2}(s + 2l_0).$$

Plotting a curve

$$\frac{t}{s} \cdot \frac{P}{\eta} \text{ versus } s$$

a straight line should be obtained, the slope being equal to $\frac{4}{R^2}$ and the intercept at $s = 0$ equal to $\frac{8l_0}{R^2}$. The linearity of the curve gives a convenient check of the uniformity and the regularity of the relevant section of the capillary.

After calibrating the instrument with oils of known viscosity, the viscosity of any liquid may be calculated from the formula :

$$\eta = \frac{tP}{s} \cdot \frac{R^2}{4s + 8l_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Corrections Applied to Pressure.

The actual pressure P under which the liquid moves consists of the summation of three pressures :

(*a*) the pressure produced by the pressure regulator p_r;
(*b*) the hydrostatic head of liquid h, in the viscometer, giving p_h;
(*c*) the capillary pressure p_c.

All three pressures act positively.

$$P = p_r + p_h + p_c$$

$$P = p_r + \rho gh + \frac{2\gamma}{R}.$$

Alternatively, if the density ρ and surface tension γ are not known approximately, the pressure correction $(p_h + p_c)$ can be determined by finding the suction pressure required to keep the meniscus stationary. Good agreement was found between the calculated and the experimental pressure correction for any one liquid.

Procedure.

The viscometer tube was cleaned by sucking through suitable solvents and finally benzene, and dried in a current of dry, dust-free air. It was then mounted securely on the frame so that the first mark on the capillary corresponded to the zero of the scale. A small drop of liquid was placed in the cup C. The rubber sleeve R, carrying the tube A, was slipped over it, the metal clamps tightened, and the whole placed into the thermostatic bath. It was left for $\frac{1}{2}$ hour, suction pressure being applied to prevent the liquid from advancing beyond the first mark. This may be used to determine the pressure correction as mentioned above. Positive pressure (approx. 10 cm Hg) was applied and the advance of the meniscus timed at every division.

Calibration.

Two highly refined mineral oils "A" and "B" were used. Their viscosity at 25° C and 37° C was measured by the ball drop method, using 50 cc test tubes and 1 mm balls falling through a tube dipping below the surface of the liquid.

Faxens correction [3] was used to correct for wall effects.

The density of the oils was also measured with a pyknometer. Table I shows the results obtained.

Table I.

Oil.	Temperature.	η corrected (poise).	ρ.
A	37° C	7·57 ± 0·04	0·877
A	25° C	18·75 ± 0·07	0·883
B	37° C	41·95 ± 0·10	0·878
B	25° C	118·8 ± 0·31	0·886

One viscometer V_1 was calibrated, using oils "A" and "B" at 25° and 37° C. The pressure applied varied between 8 and 15 cm Hg.

The pressure correction applied in both cases was 0·50 cm Hg. This is the same as the suction pressure found experimentally and is also very close to the correction $(p_h + p_c)$ calculated from the density and the surface tension (approx 25 dynes/cm), the oils being similar in character. Thus the capillary pressure correction was 0·15 cm Hg and the hydrostatic pressure correction 0·32 cm Hg ($h = 2{\cdot}5$ cm). This gives a total calculated correction of 0·47 cm Hg, which differs by 0·03 cm Hg from the experimental value of 0·50 cm Hg.

Table II shows a typical calibration run.

Fig. 3 gives the calibration line of this viscometer V_1, using the four standard viscosities shown in Table I. It was found that if the pressure correction was neglected, a straight line was obtained for each oil at a

TABLE II.

Oil "A" at 25° C. Viscometer V_1.

s.	t (secs).	p_r (cm Hg).	η (poise).	$\frac{t}{s}$ (sec cm^{-1}).	$\frac{t}{s} \cdot \frac{P^*}{\eta}$.
1	50·4	10·90	18·75	50·4	4·087 × 10^5
2	110·2	,,	,,	55·1	4·470
3	176·6	,,	,,	58·9	4·777
4	248·8	,,	,,	62·2	5·045
5	327·6	,,	,,	65·5	5·310
6	414·4	,,	,,	69·1	5·605
7	509·4	,,	,,	72·8	5·900
8	608·6	,,	,,	76·1	6·170
9	717·6	,,	,,	79·7	6·460
10	831·0	,,	,,	83·1	6·740
11	952·8	,,	,,	86·7	7·030
12	1081·8	,,	,,	90·2	7·315
13	1217	,,	,,	93·6	7·600
14	1360	,,	,,	97·1	7·875

* P expressed in dynes/sq. cm.

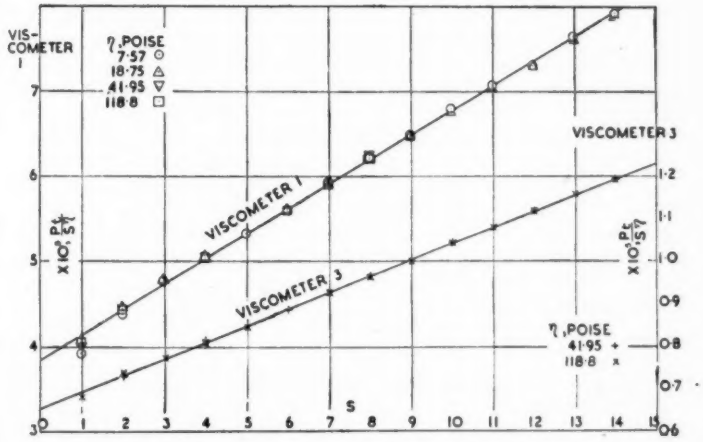

FIG. 3.

given temperature, but these did not coincide. If, however, the pressure correction is applied, the points are brought on to a single straight line, apart from scale division 1 and 2 which showed constant deviation, probably due to irregularities in the capillary.

From this experimental curve (in absolute units throughout),

$$\text{Slope} = 2{\cdot}878 \times 10^4 \text{ cm}^{-2}.$$
$$\text{Intercept} = 3{\cdot}888 \times 10^5 \text{ cm}^{-1}.$$

This gives

$$R = 0{\cdot}01179 \text{ cm}.$$
$$l_0 = 6{\cdot}75 \text{ cm}.$$

The viscosity of any liquid in the viscometer is given by

$$\eta = \frac{tP}{s} \cdot \frac{R^2}{4s + 8l_0} \quad \text{(Equation 2).}$$

The factor $\frac{R^2}{4s + 8l_0}$ is a constant for each scale division of a particular instrument and need, therefore, only be calculated once. The viscosity of a liquid is then found by multiplying the appropriate factor by $\frac{tP}{s}$ at every scale division and thus several values of the viscosity are obtained in a single run.

If the pressure P is measured in cm of mercury, the factor $\frac{R^2}{4s + 8l_0}$ must be multiplied by $1{\cdot}333 \times 10^4$.

A typical result is shown in Table III.

TABLE III.

An Opaque Liquid in Viscometer V_1.

$p_r = 13{\cdot}26$ cm Hg. $p_c + p_h = 0{\cdot}80$ cm Hg. $P = 14{\cdot}06$ cm Hg.

s (cm).	$\frac{R^2}{4s + 8l_0} \cdot 1{\cdot}333 \times 10^4$.	t (sec).	$\frac{Pt}{s}$.	η (poise).	Mean η (poise).
3	$2{\cdot}807 \times 10^{-2}$	880	4124	115·8	
4	2·646	1245	4378	115·8	
5	2·502	1642	4618	115·6	
6	2·374	2077	4867	115·7	
7	2·258	2554	5128	115·8	
8	2·153	3059	5372	115·7	
9	2·058	3601	5626	115·75	115·8 ± 0·2
10	1·971	4182	5880	115·9	
11	1·891	4793	6125	115·8	
12	1·816	5450	6385	116·0	
13	1·747	6137	6635	115·9	
14	1·683	6854	6880	115·8	

Fig. 3 also gives the calibration line of another viscometer V_3, using oil " B " at 25° and 37° C.

From this experimental curve ($p_c + p_h = 0{\cdot}40$ cm Hg) :

$$l_0 = 8{\cdot}72 \text{ cm.}$$
$$R = 0{\cdot}03237 \text{ cm.}$$

This viscometer was used for measuring viscosities between 100 and 1000 poise.

The type of viscometer described has been found useful for the detection of thixotropy or " anomalous " behaviour. Carbon black suspensions and petrol gels were investigated. As the capillary fills, the shearing stress and the rate of shear decrease, and if the viscosity is dependent on these factors an increase in the " apparent viscosity " is observed. A typical result obtained with an aluminium stearate–petrol gel is shown in Table IV. Viscometer V_3 was used to obtain the results quoted.

TABLE IV.

An Aluminium Stearate–Petrol Gel in Viscometer V_3.

$p_r = 15{\cdot}00$ cm Hg. $p_s + p_h = 0{\cdot}40$ cm Hg. $P = 15{\cdot}40$ cm Hg.

s (cm).	$\frac{R^2}{4s + 8l_0} \cdot 1{\cdot}333 \times 10^4$.	t (sec).	$\frac{Pt}{s}$.	"Apparent viscosity" (poise).
3	0·1731	217	1113	192·7
4	0·1649	308	1186	195·6
5	0·1575	407	1253	197·3
6	0·1507	524	1345	202·7
7	0·1444	651	1432	206·8
8	0·1397	780	1502	209·8
9	0·1334	949	1624	216·7
10	0·1284	1126	1731	222·3
11	0·1239	1321	1849	229·2
12	0·1197	1535	1970	235·9
13	0·1157	1764	2090	241·7
14	0·1120	2014	2216	248·1

DISCUSSION.

The microviscometer described presents certain advantages over similar instruments which have been described in the literature.[5, 6, 7] By reducing the gravity head and capillary pressure to only about 4 per cent of the total pressure applied, comparatively high accuracy can be achieved. The density and the surface tension need only be known approximately and for certain types of substances an *a priori* estimation of these constants can be made. This estimation will usually be accurate to less than 10 per cent, so that the error introduced will be less than 0·4 per cent. If the density and the surface tension of the liquid are accurately known, then the pressure correction can be calculated. A negligible error may be introduced by the fact that the shape of the advancing meniscus of the liquid may not entirely conform to the assumptions on which the calculation of the capillary pressure is based. A check on the calculations used can be obtained by observing the suction pressure to keep the meniscus stationary in the horizontal part of the capillary.

One important factor in obtaining accurate results is the observation of the position of the meniscus in the capillary. Over the relatively short distances between the scale divisions errors of parallax can easily occur. This difficulty was overcome by using the mirror scale at the back of the capillary. Not only can the scale division be observed without error, but also an enlarged image of the thread of liquid in the capillary is thrown on to the mirror scale so that the coincidence of the position of the meniscus with any scale division can be accurately observed. The mirror scale also greatly aids the correct positioning of the viscometer in the frame.

The pressure regulator used has been found satisfactory in operation. It was found slightly sensitive to large variations in room temperature. Thus a change of about 5° C may produce a change in the pressure of about 1 mm Hg. For steady temperature conditions the changes were below the accuracy of observation.

Factors like constancy of temperature, accuracy of stop-watches, and

alignment need not be discussed, since they are common to all viscometric methods.

In evaluating the experimental results the kinetic energy and Couette corrections were not applied. Calculation of the kinetic energy correction mpv^2, assuming a value of unity for m, showed that it amounted only to about 0·1 per cent even at the highest velocities used. The Couette correction (the addition of about 1 diameter to the length of the capillary) again is below 0·1 per cent and was neglected.

Generally it was found that the values of the viscosity obtained agreed within less than 0·5 per cent. With Newtonian liquids the variation observed was not systematic, showing that only errors in observation were involved. Whenever systematic variation in the values was observed, it could be traced to thixotropic or " anomalous " behaviour.

Acknowledgment.

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THE USE OF ZINC ALKYLS IN THE PREPARATION OF HYDROCARBONS WITH A QUATERNARY CARBON ATOM.

By F. R. Buck, B. B. Elsner, E. J. Forbes, S. H. Morrell, J. C. Smith, and E. R. Wallsgrove.

Synopsis.

The synthesis of several hydrocarbons containing quaternary carbon atoms was undertaken between 1942 and 1945 as an extension of an investigation started some years ago by the Anglo-Iranian Oil Co. Ltd. For these syntheses the zinc-alkyl technique was developed to give high yields.

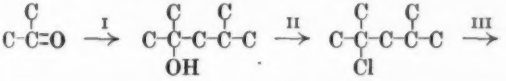
The hydrocarbons prepared were :—

2 : 2-dimethylpropane (*neo*pentane)
2 : 2-dimethylpentane
3 : 3-dimethylpentane
2 : 2-dimethylhexane
3 : 3-dimethylhexane
2 : 3 : 3-trimethylpentane
3-methyl-3-ethylpentane
2 : 3 : 3-trimethylhexane
3 : 3-diethylpentane (*neo*nonane)
3 : 3-diethylhexane
3-methyl-3-ethylheptane
1 : 1-dimethyl*cyclo*hexane
1-methyl-1-ethyl*cyclo*hexane
1-methyl-1-propyl*cyclo*hexane
1 : 1-diethyl*cyclo*hexane
1 : 2-diethyl*cyclo*hexane

A short account is also given of some side reactions, which may occur when using zinc alkyls, together with comments on a preliminary investigation into certain of these reactions.

A comprehensive investigation begun in Great Britain some years ago by the Anglo-Iranian Oil Co. included the preparation of many hydrocarbons containing a quaternary carbon atom.[1] This paper describes the use of zinc alkyls in the synthesis of such compounds.

The synthetic methods of Clarke and of Chavanne give poor results when a Grignard reagent containing a branched carbon chain has to be used.



(1)

The ketone, instead of reacting normally (Stage I, Eq. 1), may undergo self condensation, or may be reduced to a secondary alcoholic grouping.[2,3,4,5] Even if the carbinol can be obtained and converted into the tertiary halide (Stage II, Eq. 1), replacement of the halogen by an alkyl group (Stage III, Eq. 1) by use of the Grignard reagent, either fails [6,7] or proceeds with difficulty giving poor yields.

Thus in the synthesis of 2 : 2 : 3 : 3-tetramethylbutane from tertiary halides and various Grignard reagents, the yields did not exceed 10 per cent.[8]

The Wurtz reaction often gives good results in the preparation of *symmetrical* alkanes from primary and secondary halides, but fails with tertiary halides.

The use of zinc alkyls as a synthetic reagent had been largely discontinued, because of the danger involved in handling large quantities. Following Noller's [9] discovery that zinc alkyls dissolved in toluene, xylene, or tetralin could be handled in the air with relative safety, and that the yields of zinc alkyls could be increased by heating the zinc alkyl halides under reduced pressure, the availability of these reagents was greatly increased. When he showed moreover, that tertiary alkyl halides could react with zinc alkyls to give satisfactory yields of hydrocarbons, the large-scale laboratory preparation of tetra-alkyl methanes became feasible.

$$2\ \mathrm{C{-}\overset{\mathrm{C}}{\underset{\mathrm{C}}{\overset{|}{\underset{|}{\mathrm{C}}}}}{-}Br} + ZnR_2 \longrightarrow 2\ \mathrm{C{-}\overset{\mathrm{C}}{\underset{\mathrm{C}}{\overset{|}{\underset{|}{\mathrm{C}}}}}{-}R} + ZnBr_2 \quad . \quad . \quad (2)$$

Whitmore and his collaborators [8, 10] and Wibaut and co-workers [11] followed Noller's method in essential details, carrying out the coupling reactions in the region of 40 to 60°; the yields varied greatly. Noller [9] and also Wibaut [11] reported that sometimes, for unknown reasons, a violent explosion occurred. In this work, the authors have made some improvements in apparatus and technique, and have carried out many coupling reactions of zinc alkyls without the occurrence of an explosion. In cases where the hydrocarbon had been prepared before, the yields obtained by this modification were often considerably above those previously reported for successful working. In most cases, the coupling reactions should be carried out near 0°, and in all experiments further additions of alkyl halide to the zinc alkyl solution should not be made *until the first* 10 to 20 cc *have reacted*. Howard [12] also recommends keeping the temperature of reaction down to 7°.

An economic disadvantage of the large-scale use of zinc alkyls was formerly the cost of the alkyl iodides. Noller found, however, that for the preparation of zinc diethyl, equimolecular amounts of ethyl bromide and ethyl iodide could be used, whilst in our preparation of zinc dipropyl a ratio of 2 : 1, and for zinc dibutyl of 3 : 1, of bromide to iodide was used without reduction in yield.

This combination of Grignard and zinc-alkyl reactions indicates a method whereby any branched-chain hydrocarbon may be prepared.

Zinc-alkyl Technique.

Zinc dimethyl was prepared by a modification of the method used by Renshaw and Greenlaw [13] and Howard.[12] Higher zinc alkyls were prepared by the method of Noller [9, 14] with a few alterations.

A highly active zinc–copper couple was prepared by the method of Howard. 480 g of zinc dust and 60 g of copper oxide were mixed and spread evenly, in a 4-ft × 1½-in copper tube, between two plugs of asbestos wool. Hydrogen was passed through, and the tube heated to 500°; it was maintained at that temperature for 15 minutes and then allowed to

cool. The couple was stored under an atmosphere of carbon dioxide until required.

Zinc Dimethyl.

For this preparation, methyl iodide was prepared by the method of Adams and Voorhees.[15]

The apparatus used was as shown in Fig. 1. Flask " A " was fitted with a cork through which passed a separating funnel, which served as an inlet for the carbon dioxide, and a wide-bore tube for a long condenser, which had both ends bent at right-angles. The top end of the condenser passed into the side-neck of a three-necked, 2-litre flask " B." The joint was sealed with a tight, but easily removable, rubber sleeve.

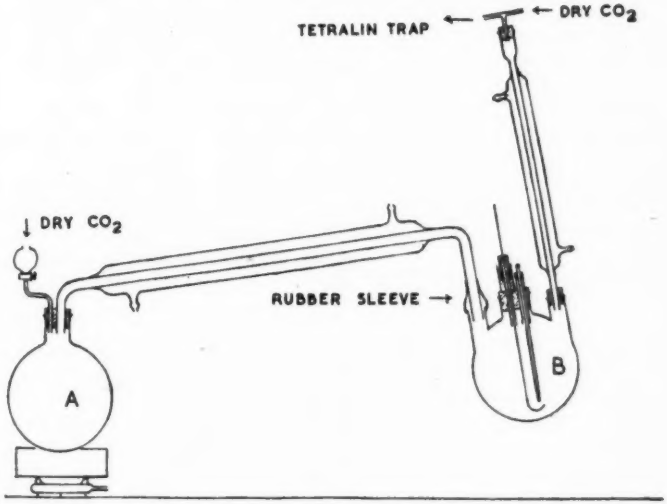


FIG. 1.

Flask " B " was fitted with a mercury-sealed stirrer, a thermometer, and a condenser at the top of which was a T-piece. One end of the T-piece was connected to a source of dry carbon dioxide, the other to a xylene or tetralin trap.

250 cc of dry xylene or tetralin were placed in flask " B " before fitting the rubber sleeve; 620 g of the zinc–copper couple together with 5 moles of methyl iodide and 2 to 4 cc of methyl acetate were placed in flask " A " and the apparatus swept out with a stream of carbon dioxide. The water bath was then heated and the liquid refluxed for 20 to 36 hours until all had turned into solid zinc methyl iodide. During this process, a slow stream of carbon dioxide was passed across the T-piece, and the flask was shaken periodically.

To convert the zinc methyl iodide into zinc dimethyl, the whole apparatus was turned through 45° so that the reflux condenser served as an ordinary

condenser, and the water bath under flask " A " was replaced by an oil bath. The zinc methyl iodide was heated to 90°, and when the bulk of the zinc dimethyl had come over the temperature was slowly raised to 200° until no more liquid distilled. After the apparatus had cooled, the rubber sleeve was slipped off and the condenser replaced by a separating funnel, through the bottom of which a stream of carbon dioxide was issuing. This stream was then shut off, the tap funnel closed, and flask " B " set in a vertical plane ready for the coupling reaction (see diagram, Fig. 2).

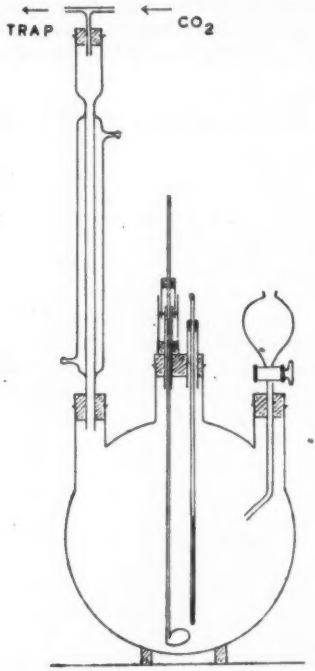


FIG. 2.

Higher Zinc Alkyls.

480 g of this zinc–copper couple were placed in a 1500 cc three-necked flask together with 2½ moles of a mixture of the iodide and bromide. The flask was fitted with two efficient condensers, and a stirrer which worked through a rubber sleeve to exclude air. At the top of one condenser was fitted a dropping funnel and to the other was fitted a T-piece, one end of which was connected to a source of dry carbon dioxide, whilst the other was open to the atmosphere through a piece of rubber tubing secured by a screw-clip.

The screw-clip was closed and the apparatus filled with carbon dioxide; the screw-clip was then opened and the carbon dioxide shut off. After

heating the flask on a water bath for a quarter to three quarters of an hour, the rate of reflux greatly increased and the water bath was removed; the reaction continued of its own accord. When the rate of reflux began to slacken, a further 2½ moles of the halide mixture was added slowly through the tap funnel. After all the halide had been added, stirring was continued until the reflux ceased. The stirrer was then lifted clear of the liquid, the carbon dioxide stream started and the flask left to cool; the stirrer and condensers were then removed, and the flask connected to a receiver and vacuum system. The receiver, a filter flask, contained a weighed amount of a suitable solvent and was cooled in a freezing mixture. The flask containing the zinc intermediate was heated on an oil bath and the zinc alkyl distilled under reduced pressure.

The iodine was recovered from the reaction flask by the method of Lachman.[16] The zinc iodide was extracted with water and filtered from the excess zinc; iodine was liberated from the aqueous extract by adding the calculated amount of potassium chlorate and concentrated hydrochloric acid. About 90 per cent of the iodine could be recovered.

A different preparation of zinc diethyl was attempted, in which ethyl chloride was passed over the zinc–copper couple at 240°. Only butane and zinc chloride resulted.

In order to economize in ethyl iodide, an aluminium catalyst [17] was prepared. 4 Moles of zinc–copper couple, 2 moles of ethyl bromide, and 10 cc of the catalyst were heated to 40° and the slow refluxing maintained. Only a 55 per cent yield of zinc diethyl was obtained.

The Coupling Reaction.

A 2-litre, three-necked flask was fitted with a dropping funnel, a thermometer, a stirrer sealed with mercury or the solvent, and a condenser, attached to the top of which was a T-piece connected to a source of dry carbon dioxide and a trap to exclude air. The apparatus was filled with dry carbon dioxide through the tap funnel; this was then removed and a known amount of zinc alkyl poured into the flask. The tap funnel was quickly replaced and the white fumes of zinc oxide allowed to settle.

Meanwhile, the apparatus was surrounded by an ice–salt bath and, when the temperature had reached 0°, 10 cc of the undiluted halide were added. In some cases there was an immediate rise of temperature indicating the start of the reaction; at other times this did not take place until one or two hours after the addition of the halide. If no rise of temperature was noticed after this time, another 10 cc of undiluted halide was added. In most cases the reaction was very noticeable, but if it was doubtful the temperature of the flask was cautiously raised, and immediately lowered when the reaction had begun.

Indications of the reaction, besides the rise in temperature, were: (*a*) formation of white fumes as the drops of halide came into contact with the vapours in the flask, and (*b*) the luminescence of the halide drops on the surface of the liquid in the flask. The drops darted around and disintegrated with a hiss.

When the reaction had begun, and only then, the rest of the halide solution dissolved in the same solvent as the zinc alkyl (1 : 1 by volume)

was added at such a rate that the temperature never rose above 3°. In some cases, the reaction temperature was kept as low as −10°. This stipulation generally allowed one mole of halide to be added per hour. Since the quantity of the zinc alkyl in the flask was known, the amount of halide necessary for the reaction was also known, allowing an excess of 10 per cent of the zinc alkyl.

After all the halide had been added, the flask was allowed to stand for a few hours, and then water was slowly added, followed by dilute acid to dissolve the zinc oxide and the precipitated zinc chloride. The upper layer was separated, washed twice with water, once with a saturated sodium bicarbonate solution, and then with water again.

After it had been dried over anhydrous sodium sulphate, the product was refluxed for 3 hours over sodium and then fractionated from sodium.

Rearrangements in Hydrocarbon Preparations.

The first type of methyl-group migration encountered in this work was in the preparation of 2 : 2-dimethylpentane from *tert*-butyl chloride and zinc dipropyl. In addition to the expected hydrocarbon, 2 : 3-dimethylpentane and 2 : 4-dimethylpentane were produced.

Noller,[9] Edgar, Calingaert and Marker,[7] and Marker and Oakwood [18] seem to have experienced the same effect in reactions with *tert*-butyl chloride, although they do not draw attention to it. It is to this cause that the authors attribute the discrepancy in physical constants reported for 2 : 2-dimethylpentane and for 2 : 2-dimethylhexane.

It was noticed, however, that on coupling the group $R-\overset{C}{\underset{C}{C}}-X$ with zinc alkyls, where R is a larger group than methyl, that no rearranged products were found. Five examples from the present work may be quoted :—

(1) $$CH_3-\overset{CH_3}{\underset{}{CH}}-\overset{CH_3}{\underset{CH_3}{C}}-Cl \xrightarrow{ZnEt_2} CH_3-\overset{CH_3}{\underset{}{CH}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$$

(2) $$CH_3-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl \xrightarrow{ZnMe_2} CH_3-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

(3) $$CH_3-CH_2-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl \xrightarrow{ZnMe_2} CH_3-CH_2-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH$$

(4) $$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl \xrightarrow{ZnEt_2} CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$$

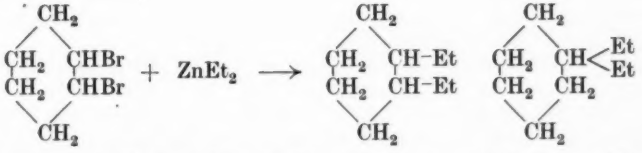
(5) $$CH_3-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl \xrightarrow{ZnEt_2} CH_3-CH_2-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$$

It is difficult to postulate any mechanism for the methyl-group migration in reactions with tertiary butyl chloride. In the case of 2 : 2-dimethylpentane, if rearrangement takes place in the tertiary butyl radical before reaction, 3-methylhexane should be present in the product. However, spectroscopic examination of the sample obtained in this work did not reveal the presence of any of this isomer. Again, it is difficult to assume that the 2 : 2-dimethylalkane should isomerize after formation, as the authors have shown that this particular end-group is stable even when treated with cold, concentrated sulphuric acid.

A methyl-group migration under the influence of cold concentrated sulphuric acid was found with 2 : 3 : 3-trimethylpentane; it isomerized completely to higher-boiling products. Migration under the influence of sulphuric acid does not occur, however, when 2-methyl or 2 : 2-dimethyl end groups are present as the only branches in the alkane chain. The grouping would always seem to rearrange, whatever the relative positions of the quaternary and tertiary carbon atoms to the methylene group.

A further instance of the migration of a side-chain methyl group occurs in the dehydration of carbinols containing a secondary or tertiary hydroxyl group adjacent to a quaternary carbon atom with one or two methyl groups attached. Brooks [19] has explained this by assuming the formation of a *cyclo*propyl ring during dehydration. Assuming that this ring could be formed, and that it could open along any of its three sides, it would give a mixture of olefines.

A further interesting example was found in the preparation of 1 : 2-diethyl*cyclo*hexane.



Spectroscopic analysis indicated the product to contain a considerable amount of the 1 : 1-isomer.

Secondary Reactions Between the Halides and the Solvents.

On purifying the solvents for their re-use, it was found that higher boiling materials were also present. These were thought to result from the interaction of the halide and the solvent, in the presence of zinc alkyls or of the anhydrous halide formed in the main reaction. In the case of 1 : 2-dibromo*cyclo*hexane and toluene the product was shown to be 2-ethyl*cyclo*hexyl-*p*-toluene, whilst in the case of *tert*-butyl chloride and xylene, the product was probably a mixture of 1 : 3-dimethyl-4-*tert*-butylbenzene and 1 : 3-dimethyl-5-*tert*-butyl benzene.

To test the hypothesis of a Friedel-Crafts type of reaction, experiments

were made with tetralin and 1-methyl-1-chloro*cyclo*hexane, with toluene and 1 : 2-dibromo*cyclo*hexane and with xylene and *tert*-butyl chloride, all in the presence of zinc chloride. No definite products were isolated.

Reducing Action of Zinc Alkyls with Tertiary Alkyl Halides.

As a by-product from the zinc-alkyl coupling reaction there was always obtained a lower-boiling fraction consisting of a mixture of olefins, formed by loss of hydrogen chloride from the tertiary halide. In an attempt to convert this lower-boiling material into the tertiary halide by addition of hydrogen halide, there was always a certain proportion of material which could not be so converted. Fractional distillation of the low-boiling material from the preparations of 3 : 3-diethylpentane, 3 : 3-diethylhexane, 3-methyl-3-ethylheptane, and 1-methyl-1-ethyl*cyclo*hexane suggested from the boiling points and refractive indices of the various fractions that it was a mixture of olefins and the corresponding paraffin. This was confirmed by hydrogenation, when the amount of hydrogen taken up indicated the lower-boiling material to be 35 to 50 per cent olefin and 65 to 50 per cent paraffin. The product so obtained was the constant-boiling paraffin corresponding to the olefin.

2 : 2-Dimethylpropane (*Neo*pentane).

Lwow [20] prepared *neo*pentane in 1870 by the action of zinc dimethyl on *tert*-butyl iodide and on 2 : 2-dichloropropane.

Ferrario and Fagetti [21] in 1908 reported the preparation of the hydrocarbon by the action of dimethyl sulphate on *tert*-butyl iodide in ether solution, and claimed a yield of 75 per cent.

The following year Maihle [22] decomposed *tert*-butyl acetic ester in the presence of freshly prepared nickel, by the method of Sabatier and Senderens,[23] to obtain *neo*pentane.

Späth [24] in 1913 used the reaction between methylmagnesium chloride and *tert*-butyl bromide to prepare *neo*pentane; he gave no yield.

In 1933, Whitmore and Fleming [25] repeated the work of the previous authors. The action of zinc dimethyl on tertiary butyl chloride, bromide, and iodide gave yields of 51, 46, and 42 per cent respectively; the decomposition of *tert*-butyl acetic ester in presence of nickel at 350° gave a 28 per cent yield; the action of dimethyl sulphate on *tert*-butyl chloride in either ether or toluene gave negligible yields of *neo*pentane; and, finally, the method of Späth gave in their hands an 18 per cent yield with *tert*-butyl bromide, and a 42 to 50 per cent yield with *tert*-butyl chloride, in toluene solution. The authors repeated the latter method two or three times, but were unable to obtain the yields claimed.

In view of the satisfactory results of the method developed here for the safe handling of zinc alkyls, Lwow's method of preparation was adopted (but using *tert*-butyl chloride, zinc dimethyl and xylene). The coupling reaction was carried out on a three-mole and a five-mole scale.

One modification was incorporated in the standard apparatus, this being the use of a trap connected to the top of the condenser, and cooled in alcohol and solid carbon dioxide. During all runs a gas was evolved

which was presumably a mixture of *neo*pentane, *iso*butene, and possibly methane, ethane, and *n*-butenes. *Neo*pentane, *iso*butene, and the *n*-butenes were retained in the cooled trap.

After the zinc chloride formed in the reaction had been dissolved in water, the product was worked up in a way different from that used in the authors' standard technique. The top of the condenser was connected to a vessel cooled in alcohol and solid carbon dioxide, the condenser itself being cooled by a rapid stream of cold water. The temperature of the reaction flask was then slowly raised by heating on a water bath, when the *neo*pentane distilled into the cooled receiver. The yield of crude *neo*-pentane was about 55 to 60 per cent. This was fractionated through a 25-plate, jacketed, Stedman column, using a total condenser cooled to −10°. The receiver was also cooled, this being maintained at a temperature of −18°, so that the hydrocarbon solidified.

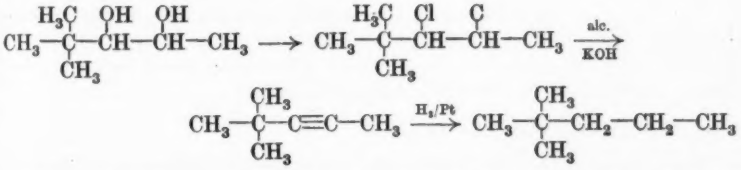
The physical properties of the product obtained were: M.p., − 15·9°, b.p. 9·5° (A.P.I. tables give b.p. 9·5° and m.p. − 16·6°).

F. R. B.
B. B. E.

2 : 2-Dimethylpentane.

The preparation of this hydrocarbon was reported by Timmermans [26] but no details were given of the method used.

The first to give any details was de Graef [27] who prepared it according to the following scheme :—



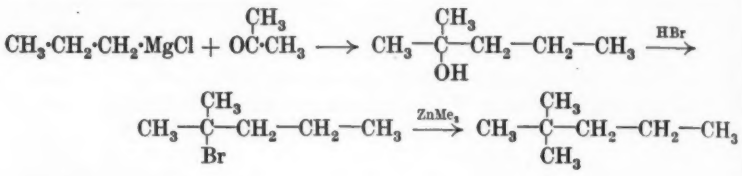
Edgar, Calingaert, and Marker [7] prepared this hydrocarbon by the action of *tert*-butyl chloride on *n*-propylmagnesium chloride with mercuric chloride as catalyst, and reported a yield of 21 per cent. Their attempt to prepare 2 : 2-dimethylpentane by the dehydration of 2 : 2-dimethylpentan-3-ol, followed by reduction of the olefins, did not succeed because a mixture of 2 : 2-dimethyl pentane and 2 : 3-dimethylpentane was obtained.

Wibaut [11] prepared 2 : 2-dimethylpentan-3-ol by the method of Edgar and his collaborators, and dehydrated it by passing the acetate over glass wool at 400° (compare Cramer and Mulligan [28]). This gave only 4 : 4-dimethylpenta-2-ene, which on hydrogenation yielded 2 : 2-dimethylpentane.

Noller [9] prepared this hydrocarbon by the action of zinc dipropyl on *tert*-butyl chloride in xylene solution, and obtained a product of b.p. 80 to 81°. The authors repeated Noller's method and obtained a product which boiled over a range, and was shown by infra-red spectroscopy to be a mixture of 2 : 2-dimethylpentane (b.p. 79·0°), 2 : 3-dimethylpentane

(b.p. 89·7°), and 2 : 4-dimethylpentane (b.p. 80·8°). It seemed that this rearrangement of the 2 : 2-dimethylpentane skeleton during the reaction had escaped Noller's notice. As it was not practicable to separate the hydrocarbons, this method of preparation had to be rejected in favour of an alternative.

2-Methylpentan-2-ol was prepared by the action of acetone on *n*-propylmagnesium chloride, followed by the conversion of the product to 2-methyl-2-bromopentane; this bromide was coupled with zinc dimethyl to give the required hydrocarbon. No rearranged products were found in the sample so obtained.



2-Methylpentan-2-ol.

The Grignard reaction was carried out in the usual way. The distillation of the carbinol had to be carried out at reduced pressure; this method gave a yield of 76 per cent, as opposed to 68 per cent, the highest yield obtained by normal pressure distillation.

2-Methyl-2-bromopentane.

Conversion of the carbinol to the bromide was carried out by passing hydrogen bromide into it until no more was absorbed; anhydrous calcium chloride was also placed in the flask to absorb the water formed. The yield obtained was 84 per cent; b.p. 66·8°/84 mm.

Coupling Reaction with Zinc Dimethyl.

The first attempt was made with zinc methyl iodide by a method essentially that of Schlenk,[29] using xylene as a solvent. In view of the small yield and obvious impurity of the crude hydrocarbon, it was decided to use zinc dimethyl in further coupling reactions.

Xylene was used as solvent and the coupling proceeded smoothly. On distilling the xylene solution, the following lower-boiling fractions were obtained from a five-mole run :—

Fraction.	B.p., ° C.	Volume, cc
1	72–74	40
2	74–77	70
3	77–79	395
4	79–84	75
5	xylene	—

The fractions still containing bromine were refluxed over sodium wire for about 6 hours; the liquid was filtered from the brown precipitate, and shaken for 12 hours over concentrated sulphuric acid to remove unsaturated

products. After washing with water, sodium bicarbonate solution, and warer again, the liquid was dried over anhydrous sodium sulphate, refluxed over sodium wire, and finally distilled in the presence of sodium, giving a yield of 42 per cent of pure 2 : 2-dimethylpentane; b.p. 79·0°/760 (corr.); n_D^{30} 1·3821. The best figures given by the A.P.I. for these two physical properties are : 79·205°/760 mm and 1·38217, respectively.

F. R. B.
B. B. E.

3 : 3-Dimethylpentane.

Friedel and Ladenburg [30] set out to prepare this compound as early as 1867, from 2 : 2-dichloropropane and zinc diethyl. They reported the coupling to be fairly troublesome, but they obtained a heptane of b.p. 86 to 87°.

The next occurrence in the literature was when De Montmollin [31] reported it as one of the products of the action of phosphoric acid on ethyl alcohol at 200°.

No other preparations of this heptane were recorded until comparatively recently, when Noller [9] in his syntheses with zinc alkyls (1929) obtained it in 51 per cent yield from *tert*-amyl chloride and zinc diethyl.

Edgar, Calingaert, and Marker,[7] after making several attempts to prepare this hydrocarbon by the method of Chavanne, and finding that the alcohols rearranged on dehydration, finally coupled ethylmagnesium bromide with *tert*-amyl chloride to obtain a 13 per cent yield of the desired product.

Schurmann and Boord prepared this heptane from 3 : 3-dimethylpentan-2-ol by means of their " xanthic ester synthesis."

Marker and Oakwood [18] coupled *tert*-amyl chloride with ethylmagnesium bromide in ether solution, using cuprous iodide as catalyst, and obtained a 22 per cent yield of 3 : 3-dimethylpentane.

Wibaut and his collaborators [11] stated that they had been unable to repeat the preparation given by Edgar, Calingaert, and Marker (*loc. cit.*), and that they had used the method of Noller. They recorded that on one occasion the temperature rose rapidly and caused a vigorous reaction which destroyed the apparatus and led to a fire. In this work too, the method of Noller was followed ; by taking care that the temperature of the reaction mixture was always slightly above the temperature of the outside of the flask, the reaction was carried out at 4° with perfect safety.

Tert-*amyl chloride*.

This was prepared by the method of Norris, Watt, and Thomas.[33] It was found that the *tert*-amyl chloride decomposed on distillation at normal pressure; by carrying out the distillation at reduced pressure, however, a product of constant boiling point was obtained. The organic layer was washed twice with water and once with sodium bicarbonate solution. After this layer had been separated and dried over calcium chloride or phosphorus pentoxide for two days, it was distilled through a 30-cm Dufton column at 550 mm. Only a small quantity (5 per cent) of low-boiling material (44 to 48°) was obtained and the remainder of the material came over at 48·5 to 49·5°.

The *coupling reaction* was carried out in xylene solution by the standard technique.

The product was distilled through a 30-cm Dufton column and the following fractions were obtained :—

(*a*) 0 to 80°, mainly a mixture of olefins.

(*b*) 80 to 87°, main fraction, containing some unchanged chloride.

The chloride was removed from the main fraction by refluxing for 8 hours over sodium wire; the fraction was then purified by shaking with concentrated sulphuric acid for 24 hours. The product was washed, dried, and refluxed over sodium–potassium alloy, after which it was distilled through a 60-cm Dufton column, when the following fractions were obtained from a combined three-mole and two-mole run of the chloride :—

	B.p., ° C.	Quantity.	n_D^{20}.
(*a*)	85 –86	20 cc	—
(*b*)	86 –86·15	50 ,,	1·3910
(*c*)	86·2	240 g	1·3911
(*d*)	86·2–86·4	30 cc	—

The distillation was carried out at 769 mm. Fraction (*c*) represented a yield of 48 per cent of 3 : 3-dimethylpentane, b.p. 85·8°/760 mm, n_D^{20} 1·3911. A.P.I. Tables give b.p. 86·071° and n_D^{20} 1·39090.

Using three moles of *tert*-amyl chloride a coupling reaction at higher temperature was carried out at 50 to 60°. The organic layer was worked up and purified as before, yielding on distillation the following fractions :—

	B.p., ° C.	Quantity.	n_D^{20}.
(*a*)	85–86	20 cc	—
(*b*)	86–86·15	30 ,,	1·3910
(*c*)	86·2	70 g	1·3911

Fraction (*c*) represented a yield of only 23 per cent.

B. B. E.
S. H. M.

2 : 2-Dimethylhexane.

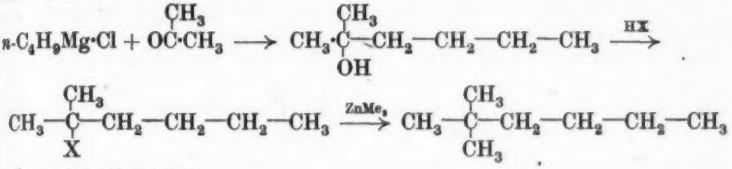
This hydrocarbon was prepared by Noller [9] by the action of *tert*-butyl chloride on zinc di-*n*-butyl in tetralin solution. He stated that the octane was obtained in 36 per cent yield, having the physical constants b.p. 106 to 107°, n_D^{20} 1·3931. From the comparatively wide boiling range he gave, and in view of the authors' experience with *tert*-butyl chloride, it would seem probable that migration of the methyl groups had occurred during the coupling reaction, and that he had obtained isomers of 2 : 2-dimethylhexane as well as the expected product.

The next recorded preparation was that of Schurmann and Boord,[32] who reduced 2 : 2-dimethylhexa-3-ene, obtained from the methyl xanthate of 2 : 2-dimethylhexan-3-ol by heating under reflux.

Maman [34] also reported the preparation of this hydrocarbon, but gave no details of the method used.

Whitmore and Zook[35] have obtained 2 : 2-dimethylhexane in 4 per cent yield by the action of sodium propyl on *neo*pentyl chloride, the main product being 1 : 1-dimethyl*cyclo*propane.

The method adopted for the preparation of this hydrocarbon was as follows :—



where X is Br or Cl.

When 2-methyl-2-bromohexane was used, a 32 per cent yield was obtained, but the corresponding *chloride* gave a 50 per cent yield of 2 : 2-dimethylhexane.

2-*Methylhexan*-2-*ol* was prepared from *n*-butylmagnesium chloride and acetone in a yield of 83 per cent; b.p. 68·5°/35 mm.

2-*Methyl*-2-*bromohexane* was prepared from the carbinol by the method used for 2-methyl-2-bromopentane. The main distillate, obtained in a yield of 84 per cent, boiled at 59°/25 mm., and had a refractive index n_D^{20} 1·4472. This compound had not been reported before. On analysis it gave Br, 44·38 per cent; $C_7H_{15}Br$ requires Br, 44·69 per cent.

2-*Methyl*-2-*chlorohexane* was prepared by a modification of the method of Norris and Olmsted.[36] Instead of using hydrochloric acid, a mixture of the latter and sulphuric acid (50 cc of concentrated sulphuric acid and 6 moles of hydrochloric acid) was used. The chloride was obtained in 89 per cent yield; b.p. 35·9°/16 mm, n_D^{20} 1·4202.

The coupling reactions were performed by the standard technique in tetralin solution; tetralin was used as solvent as xylene proved difficult to separate from the paraffin. In a preparation using 4 moles of the chloride, the tetralin solution, after being washed and dried, was fractionated. As fuming was noticed during the distillation, due to loss of hydrogen chloride from the excess 2-methyl-2-chlorohexane, the fractions were united and refluxed over sodium for eight hours. The hydrocarbon, after being filtered, washed and dried, distilled as follows :—

Fraction.	B.p., ° C.	Volume, cc.
1	102–105	8
2	105–106	18
3	106–107	40
4	107	260
5	107–110	7

Fractions 2 to 5 were redistilled through a 90-cm Dufton column, using a McIntyre pattern still-head and standard thermometer; b.p. 106·9°/760 mm, n_D^{20} 1·3934.

A.P.I. Tables give b.p. 106·843 and n_D^{20} 1·39349.

F. R. B.
B. B. E.

3 : 3-Dimethylhexane.

The first recorded preparation was that of Späth [6] who formed this hydrocarbon in 15 per cent yield by coupling *tert*-amyl halides with *n*-propylmagnesium halides.

Noller [9] prepared it from zinc di-*n*-propyl and *tert*-amyl chloride, and recorded a yield of 24 per cent of a substance of b.p. 111 to 112°.

Schurmann and Boord [32] next prepared it by dehydrating the xanthic ester of the corresponding carbinol $CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}(OH)\cdot CH\cdot CH_2CH_3$—and recorded that the olefin $CH_3\cdot CH_2\cdot\overset{CH_3}{\underset{CH_3}{C}}=CH\cdot CH_3$ was obtained in 25 per cent yield based on the carbinol used.

Marker and Oakwood [18] employed a similar method to that which they had used for 3 : 3-dimethylpentane and recorded a yield of 17 per cent.

The authors followed the method of Noller, but used 2-methyl-2-bromopentane and zinc diethyl in place of the reagents he employed. The use of these reagents, and of a lower temperature in the coupling reaction, doubled the yield. The complete reaction scheme was as follows :—

$$n\text{-}C_3H_7MgCl + \overset{CH_3}{\underset{}{O}}C\cdot CH_3 \longrightarrow CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2-CH_2-CH_3 \xrightarrow{HBr}$$

$$CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_2-CH_3 \xrightarrow{ZnEt_2} CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2-CH_3$$

2-Methylpentan-2-ol was prepared by the method of Wibaut [11] except that propyl chloride was used in place of the bromide. The yield of product, of b.p. 92°/100 mm and n_D^{20} 1·4114, was 64 per cent of the theoretical. Only the pure carbinol could be distilled under atmospheric pressure without decomposition; b.p. 122°/760 mm.

2-Methyl-2-bromopentane was prepared as described under 2 : 2-dimethylpentane; b.p. 70°/100 mm, n_D^{20} 1·4440, n_D^{23} 1·4428; yield 82 per cent.

The coupling reaction was carried out in tetralin solution at 3 to 6°. The product was fractionated through a 30-cm Dufton column and gave between 60 and 70° two quite distinct fractions, these being 2-methylpenta-1-ene (b.p. 61°) and 2-methylpenta-2-ene (b.p. 67°). The main fractions came over at 111 to 114°. Two 3-mole runs and a 1½-mole run yielded 500 cc of this fraction. After refluxing it over sodium for 4 hours and then shaking it twice with concentrated sulphuric acid, the hydrocarbon was washed, dried, and fractionated from sodium through a 60-cm Dufton column, giving a total yield of 315 g of 3 : 3-dimethylhexane (40 per cent yield) of b.p. 111·9°/760 mm, n_D^{20} 1·4004.

A.P.I. Tables give b.p. 111·972° and n_D^{20} 1·40009.

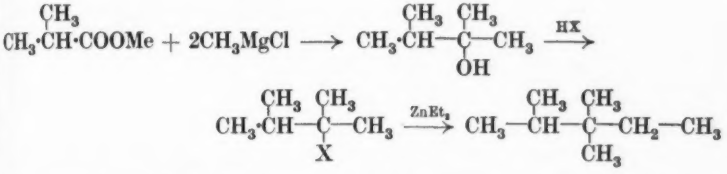
B. B. E.
S. H. M.

2 : 3 : 3-Trimethylpentane.

This hydrocarbon has been reported in the literature by Laughlin and Whitmore,[37] and by Maman.[38] The former workers prepared methyl *tert*-amyl ketone by the Grignard reaction between acetyl chloride and *tert*-amylmagnesium chloride; they then converted the ketone to dimethyl *tert*-amyl carbinol by the action of methylmagnesium chloride. Dehydration of the carbinol gave 2 : 3 : 3-trimethylpenta-1-ene, which was reduced to 2 : 3 : 3-trimethylpentane. The reference to Maman's work was not available.

Wibaut *et al* [39] obtained this hydrocarbon as a by-product in the preparation of 2 : 2 : 3-trimethylpentane.

The scheme of our method of preparation was as follows :—



*Iso*butyric ester, obtained from methyl methacrylate by catalytic reduction, was coupled with methylmagnesium chloride. The average yield of the resulting carbinol, 2 : 3-dimethylbutan-2-ol, was 59 per cent, b.p. 119°/760 mm.

2 : 3-*Dimethyl*-2-*bromobutane* was prepared from the carbinol using the method described on p. 348; b.p. 79—82°/555 mm.

2 : 3-*Dimethyl*-2-*chlorobutane* was prepared by another variation of the method of Norris and Olmsted.[36] The main fraction boiled at 111·1 to 112·2/755 mm with slight decomposition into olefin and hydrochloric acid. On distillation of the chloride at reduced pressure no hydrogen chloride was evolved and, except for a small initial and a small tail fraction, the whole boiled at 71·5°/555 mm; m.p. − 7·2°, f.p. − 7·5°. The constants were the same as those obtained for the material of b.p. 111·1 to 112·2°/755 mm.

The coupling reaction was carried out in tetralin solution according to our standard technique; the product obtained distilled as follows :—

Fraction.	B.p., ° C.	Volume, cc.
1	58–74	180
2	74–114	15
3	over 114	190

Fraction 1 was a mixture of 2 : 3-dimethylbuta-1-ene, 2 : 3-dimethylbuta-2-ene and 2 : 3-dimethylbutane, being about 50 per cent paraffin. Fraction 3 was approximately a 50 per cent yield of the crude octane, based on the chloride.

When the crude 2 : 3 : 3-trimethylpentane was shaken with concentrated

sulphuric acid for sixteen hours the acid turned a very brown colour, and on being diluted gave an unusually large amount of sulphur. After the hydrocarbon had been washed and dried, it was distilled; distillation did not start until 124°, showing complete disruption of the molecule.

The above method of preparation was repeated, with a view to isolating the pure octane by fractionation of the crude hydrocarbon.

200 g of zinc diethyl were coupled in tetralin solution with 2 : 3-dimethyl-2-chlorobutane, until no further rise in temperature could be observed. The reaction mixture was decomposed and the tetralin solution washed, dried, and distilled.

Fraction.	B.p., ° C/760 mm.	Volume, cc.	n_D^{20}.
1	45·1– 58·4	48	1·3774
2	58·4– 65·0	75	1·3829
3	65·0– 72·9	75	1·3990
4	72·9–114·0	70	>1·40
5	114·0–114·8	135	,,
6	over 114·8	30	,,

The refractive index of fraction 1 suggested that it was practically pure 2 : 3-dimethylbutane contaminated with a little 2 : 3-dimethylbuta-1-ene, whilst fractions 2 and 3 were mixtures of the hexane with 2 : 3-dimethylbuta-1-ene and 2 : 3-dimethylbuta-2-ene respectively.

Fraction 4 was redistilled and the higher-boiling part combined with fractions 5 and 6, and the whole fractionated through a 60-cm Dufton column. The following distillation data were obtained :—

Fraction.	B.p., ° C/745 mm.	Volume, cc.	n_D^{20}.
1	105·4 –113·4	18	1·4072
2	113·4 –113·85	15	1·4076
3	113·85	75	1·4076
4	113·85–114·0	34	1·4076
5	114·0 –114·5	18	1·4079

The physical constants for this hydrocarbon are thus : b.p./760 mm, 114·6° C; n_D^{20}, 1·4076.

A.P.I. Tables give b.p. 114·763° and n_D^{20} 1·40752.

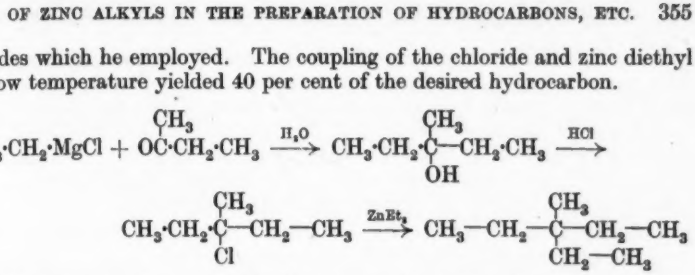
F. R. B.
B. B. E.

3-Methyl-3-ethylpentane.

The earliest recorded preparation of this hydrocarbon was that of Tafel and Jurgens,[40] who obtained it in 41 per cent yield by the electrolysis of diethylacetoacetic ester. No further method of preparing this hydrocarbon was described until 1939, when Wibaut [11] obtained it in 15 per cent yield by the action of zinc diethyl on 3-methyl-3-iodopentane.

The method used in this preparation closely followed that of Wibaut, except that chloro compounds were used in place of the bromides and

iodides which he employed. The coupling of the chloride and zinc diethyl at low temperature yielded 40 per cent of the desired hydrocarbon.



3-*Methylpentan*-3-*ol* was prepared from ethylmagnesium chloride and methylethyl ketone; b.p. 121 to 123°/760 mm, n_D^{20} 1·4182 to 1·4184.

3-*Methyl*-3-*chloropentane* was prepared from the carbinol in 70 per cent yield by shaking it with concentrated hydrochloric acid; b.p. 69—70°/150 mm, n_D^{20} 1·4207, $n_D^{16\cdot5}$ 1·4225.

The coupling reaction was performed in 4-mole runs in tetralin solution by the standard technique; the product was distilled through a 30-cm Dufton column. Between 60 and 69°, 100 cc of olefin came over, this being a mixture of the three possible olefins: *cis*- and *trans*-3-methylpenta-2-ene (b.p. 66° and 69° respectively) and 2-ethylbuta-1-ene (b.p. 66°). Then the temperature rose rapidly to 116° when a mixture of the octane and traces of the hexenes came over. The yield of the hexenes was approximately 32 per cent, and that of the crude octane 60 per cent.

After the crude octane had been refluxed for 4 hours over sodium, the liquid was shaken with concentrated sulphuric acid for 6 hours. The final distillation of the hydrocarbon, from the above run together with a second run using 3·25 moles of halide, through a 60-cm Dufton column from sodium wire, yielded a main fraction of 340 g; b.p. 118·05°/760 mm (corr.); n_D^{20} 1·4080. The b.p. and refractive index were in close agreement with the values given by the previous workers.

A.P.I. Tables give b.p. 118·262° and n_D^{20} 1·40775.

B. B. E.
S. H. M.

2 : 3 : 3-Trimethylhexane.

This nonane has been prepared by Cline.[41] No description of his method was available and the physical constants which he obtained differed from those recorded here.

The authors obtained the hydrocarbon by a method analogous to that used for 2 : 3 : 3-trimethylpentane, using zinc dipropyl in place of zinc diethyl. Our product had the following constants: b.p. 136·8°/760 mm (corr.); n_D^{20} 1·4149. Cline (*loc. cit.*) gave b.p. 137·4 to 137·6°, n_D^{20} 1·4141.

A.P.I. Tables give b.p. 138·000 and n_D^{20} 1·4143.

Coupling Reaction.

The coupling reaction was carried out with 274 g of zinc dipropyl and 395 g (3·27 moles) of 2 : 3-dimethyl-2-chlorobutane (b.p. 71·5°/555 mm). The reaction started immediately at room temperature, and the flask was cooled to 0°, and finally — 15°. It was found that at the latter temperature the reaction proceeded smoothly, and it seems that in this case

cooling in solid carbon dioxide and alcohol would give even higher yields. The product was worked up in the usual manner, refluxed over sodium for 6 hours to remove a slight excess of the chloride, and fractionated.

A few cc of distillate came over at 55° (b.p. of 2 : 3-dimethylbuta-1-ene, 55·8°), then 100 cc of nearly constant b.p. 58° (b.p. of 2 : 3-dimethylbutane 58°); the temperature then rose to 66° and finally to 73°, giving a fraction of 80 cc (b.p. of 2 : 3-dimethylbuta-2-ene 73·3°).

The main fraction (120 g) boiled at 134 to 136°/759 mm giving a 34 per cent yield of crude hydrocarbon based on the chloride.

The main fraction was redistilled through a 25-plate Stedman column when the following fractions were obtained :—

	cc.	n_D^{20}.
(1) Up to 134·2°/733 mm . .	6	—
(2) 134·2–135·4°/733 mm . .	8	1·4145
(3) 135·4–135·6°/733 mm . .	10	1·4149
(4) 135·6 const./733 mm . .	115	1·4149
Residue	10	

From the 3·27 moles of chloride used one mole was transformed into the nonane and 2 moles decomposed to give the olefins. The olefin with the terminal double bond was present only in a small quantity, which means that the decomposition took place in favour of the other olefin or that the former was more readily reduced. The main part of the lower-boiling material consisted of 2 : 3-dimethylbutane.

B. B. E.

3 : 3-Diethylpentane.

This important nonane (carbon tetraethyl) is described in the literature only by Morgan, Carter, and Duck.[42]

The interaction of zinc diethyl and triethyliodomethane without a solvent (as described by Morgan, Carter, and Duck) gave in our hands very poor yields of the nonane. Poor results were also obtained from the triethylchloromethane and zinc diethyl in tetralin solution by the standard technique, but the corresponding bromide reacted smoothly at 0 to 4° in tetralin solution, giving 32 per cent yields of the desired product. The complete scheme was :—

$$CH_3{\cdot}CH_2{\cdot}COOEt \xrightarrow[H_2O]{EtMgCl} CH_3CH_2\overset{\displaystyle Et}{\underset{\displaystyle Et}{C}}{-}OH \xrightarrow{HBr}$$

$$CH_3CH_2\overset{\displaystyle Et}{\underset{\displaystyle Et}{C}}{-}Br \xrightarrow{ZnEt_2} CH_3CH_2\overset{\displaystyle Et}{\underset{\displaystyle Et}{C}}{-}Et$$

By-products of the reaction with zinc diethyl were an olefin (probably 3-ethylpenta-2-ene, formed by loss of hydrogen bromide from triethylchloromethane) and 3-ethylpentane by reduction of the olefin. Because of its symmetry carbon tetraethyl is relatively high melting (— 32·3°). The physical constants recorded in this work differ considerably from those given by Morgan, Carter, and Duck (*loc. cit.*).

Triethylbromomethane.

Dry hydrogen bromide was passed into a separating funnel containing triethylcarbinol (for preparation see the synthesis of 3-ethylpentane), as long as the gas was absorbed, and the lower layer removed periodically. On washing with water the organic layer became the lower layer; it was washed with sodium bicarbonate solution, with water again and dried with calcium chloride. On distillation 75 per cent yields of bromide, b.p. 98 to 100°/100 mm and n_D^{20} 1·4600 to 1·4606, were obtained. Redistillation at 97°/90 mm gave a product of n_D^{20} 1·4609. (Found: Br, 43·9 per cent: $C_7H_{15}Br$ requires Br, 44·7 per cent.)

Reaction with zinc diethyl. A solution of 220 g (1·8 mole) of zinc diethyl dissolved in 200 g of tetralin was cooled to 1° by surrounding the flask with ice water, and then a solution of triethylbromomethane (540 g, 3 moles) in 540 cc of tetralin was added at such a rate as to maintain a reaction temperature of 4° until the sudden fall occurred at the finish. Water (300 cc) was added to dissolve the zinc chloride, then 400 cc of dilute sulphuric acid (10 per cent). The organic layer was washed with water, sodium bicarbonate solution, water again, and dried over sodium sulphate. Distillation through a 30-cm Dufton (Quickfit) column gave first a fraction of b.p. 96 to 98°/760 mm and then, at 550 mm, a large fraction b.p. 118 to 120°; redistillation of the lower fractions gave more of the 118 to 120°/550 mm fraction, which was crude 3 : 3-diethylpentane. The crude diethylpentane (370 cc) from two reactions on this scale with zinc diethyl was distilled through a 60-mm Dufton (Quickfit) column yielding :—

	M.p.	n_D^{20}.
Fraction (*a*) up to 145° . . .	−40°	—
,, (*b*) 145·2 to 145·35° . .	−33·7 ± 0·5°	1·4204
,, (*c*) 145·3 to 145·35° . .	−32·8	1·4205
,, (*d*) 145·35 to 145·5° . .	−33·0	1·4205

The total yield of product b.p. 145 to 145·5° was 255 g (32 per cent). Fraction (*c*) was partly frozen, the liquid drained away, and the solid found to melt at − 32·8°. As Morgan, Carter, and Duck (*loc. cit.*) gave m.p. − 41° and b.p. 139·2° (Siwoloboff's method) for their 3 : 3-diethylpentane which had been purified by shaking with conc sulphuric acid fraction (*c*) was shaken for a short time with conc sulphuric acid and then for 3 hours with its own volume of fuming sulphuric acid (10 per cent SO_3). The product then melted at − 32·6°; on distillation it yielded a middle fraction of b.p. 144·8°/746 mm (145·7°/760 mm), m.p. − 32·6° ± 0·5° and n_D^{20} 1·4203. (Found: C, 84·1; H, 15·85 per cent. Calc. for C_9H_{20}: C, 84·4; H, 15·6 per cent). Dr L. A. K. Stavely of the Department of Inorganic Chemistry kindly took the m.p. of this sample with an accurate thermo-couple and found the value to be − 33·05° ± 0·05°. Horton [42a] gave m.p. − 31·1°; b.p. (Cottrell) 146·4°; n_D^{20} 1·4203, but Rossini [42b] recorded m.p. − 33·110° ± 0·005°; n_D^{25} 1·4182.

(This hydrocarbon is difficult to combust, and should be burnt slowly with a hot tube-filling.)

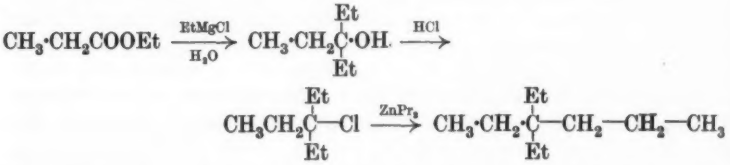
Examination of the low-boiling fraction (b.p. 96 to 98°) showed that it

was unsaturated and reaction with hydrogen bromide gave back triethylbromoethane of n_D^{20} 1·4593. But a saturated hydrocarbon of b.p. approximately 93° accompanied the bromide. Reduction of the original 96 to 98° fraction with hydrogen and Raney nickel at 180° and 100 atm pressure gave a product of b.p. 92·8 to 93·3°, main fraction 93·2 to 93·3°/759 mm, n_D^{20} 1·3935. Egloff [43] gives for 3-ethylpentane b.p. 93·3°/760 mm and $n_{D_r}^{20}$ 1·3934.

S. H. M.
J. C. S.

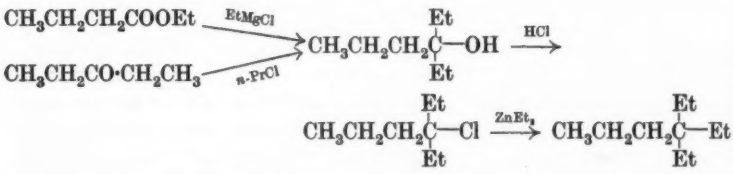
3 : 3-Diethylhexane.

The synthesis of this decane has not prevously been recorded. An attempt was made to prepare it by the following procedure :—



The coupling reaction between 3-chloro-3-ethylpentane and zinc dipropyl in tetralin solution did not give a product of sharp boiling point. When the low-boiling fraction was reduced, it took up an amount of hydrogen corresponding to a mixture of 60 per cent of 3-ethylpentane and 40 per cent of 3-ethylpenta-3-ene.

A second method proved more successful :—



Diethyl Ketone was made both by the passage of propionic acid over thoria on pumice at 440° in 50 per cent yield and by the pyrolysis of calcium propionate (60 per cent yield).

Ethyl-n-*butyrate* was obtained by refluxing butyric acid and ethyl alcohol with a small amount of conc sulphuric acid for 8 hours.

3-*Ethylhexan*-3-*ol* was obtained in a yield of 70 per cent from ethyl butyrate and ethyl magnesium chloride and in a 65 per cent yield from diethylketone and *n*-propylmagnesium chloride, b.p. 78 to 80°/40 mm, n_D^{20} 1·4300. At atmospheric pressure it boiled at 154 to 155°/752 mm, some decomposition taking place.

3-*Chloro*-3-*ethylhexane* was obtained in 94 per cent yield when 3-ethylhexan-3-ol was cooled in ice and gaseous hydrogen chloride passed in for three hours. B.p. 62 to 63°/24 mm, 78 to 79°/46 mm; n_D^{20} 1·4358. Found : Cl, 23·30 per cent; calc for $C_8H_{17}Cl$: Cl, 23·90 per cent.

The coupling reaction with zinc diethyl in tetralin started at once, the thermometer recording a rise of 20°. The product was distilled through a 30-cm Dufton column giving a main fraction b.p. 165·8 to 166·8°/750 mm representing a yield of 40 per cent. Redistillation of this fraction gave the required decane; b.p. 166·2 to 166·3°/760 mm (corr.); n_D^{20} 1·4246.

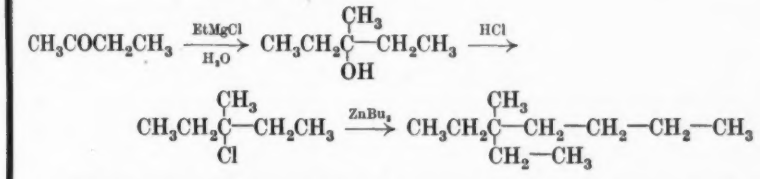
Reduction of the low boiling fraction gave 3-ethylhexane; b.p. 118·2 to 118·4°, n_D^{20} 1·4018.

B. B. E.
E. R. W.

3-Methyl-3-ethylheptane.

The only preparation of this decane recorded in the literature is that of Campbell and Eby [44] who reduced 3-methyl-3-ethylhepta-4-yne. The acetylene was made from 3-methylhepta-4-yne-3-ol, the product of the interaction of buta-1-yne and methyl ethyl ketone in liquid ammonia. The acetylenic carbinol was converted to the chloride and this, by interaction with ethylmagnesium chloride, gave the 3-methyl-3-ethylhepta-4-yne.

The physical constants recorded by Campbell and Eby do not agree with those of the hydrocarbon prepared in this work by the action of zinc di-*n*-butyl on 3-chloro-3-methylpentane :—



3-*Methylpentan*-3-*ol* was obtained from methyl ethyl ketone and ethyl magnesium chloride in 65 per cent yield. The carbinol was converted to 3-chloro-3-methyl pentane (90·5 per cent yield; b.p. 116·5 to 118°, n_D^{20} 1·4205) [45] and the latter coupled with zinc di-*n*-butyl in tetralin solution by our standard technique. The solution was cooled in a freezing mixture of ice and salt. A few cc of the chloride was added. This failed to produce any rise in temperature or any sign of reaction; nor did addition of a little of the undiluted chloride. The reaction had finally to be conducted cooled in iced water, with the internal temperature kept at between 10 and 20° by adjustment of the rate of addition. The product was distilled through a 30-cm Dufton column and the middle fraction redistilled through two 30-cm Dufton columns giving a 23 per cent yield of 3-methyl-3-ethylheptane, b.p. 162·9 to 163·9°/752 mm. Redistillation of the decane yielded the main fraction of the required hydrocarbon boiling at 163·7 to 163·9°/760 mm (corr.), n_D^{20} 1·4208. Found : C, 84·55 per cent; H, 15·63 per cent. Calc for $C_{10}H_{22}$, C, 84·51 per cent; H, 15·49 per cent. Campbell and Eby gave the following constants : b.p. 155°/737 mm; n_D^{20} 1·4179.

As with the previous preparation the lower-boiling fraction b.p. 63 to 66° showed, from the boiling point and refractive index, indications of being a mixture of paraffin and olefin. Hydrogenation with Raney nickel

as catalyst and hydrogen under 110 atmospheres at 170° indicated that roughly 50 per cent of the mixture was olefin, 3-methylpentane, b.p. 63·1°/760 mm, being the sole product of the reduction.

B. B. E.
E. R. W.

1 : 1-Dimethyl*cyclo*hexane.

The preparation of this compound by an unequivocal method was first reported by Crossley and Renouf.[46] Starting from dimedone, which behaves in many respects as a monohydroxy-compound, they prepared the chloroketone by the action of phosphorus trichloride. Reduction with sodium in moist ether gave 1 : 1-dimethyl*cyclo*hexan-3-ol which was converted into the bromide. Reduction of the latter was accomplished with zinc dust.

Next followed a simpler preparation from dimedone by Zelinsky.[47] Reduction with sodium in alcohol gave 1 : 1-dimethyl*cyclo*hexan-3 : 5-diol, and this was converted into the 3 : 5-dibromo compound with phosphorus pentabromide. Reduction to the required hydrocarbon was accomplished by the use of a zinc–platinum catalyst.

Chavanne, Miller, and Cornet[48] prepared 1 : 1-dimethyl*cyclo*hexane by a method similar to that of Crossley and Renouf. The monochloro compound of dimedone was reduced with a nickel catalyst, giving a 30 per cent yield of 1 : 1-dimethyl*cyclo*hexan-3-ol. This latter was dehydrated with *p*-toluenesulphonic acid and the resulting olefins hydrogenated.

In 1936 Zelinsky[49] converted dimedone directly and quantitatively to 1 : 1-dimethyl*cyclo*hexan-3-ol by reducing its alcoholic solution or aqueous suspension with hydrogen under slight pressure (50 cm of water) using activated charcoal, which had been previously shaken in a solution of chloroplatinous acid in hydrogen. The carbinol was dehydrated with potassium bisulphate and the resulting mixture of olefins hydrogenated.

Five years later, Wibaut and Gitsels[50] reduced dimedone directly to 1 : 1-dimethyl*cyclo*hexane in 10 per cent yield. The dimedone was dissolved in ethyl alcohol containing 1 per cent of hydrochloric acid, and platinum oxide was used as a catalyst.

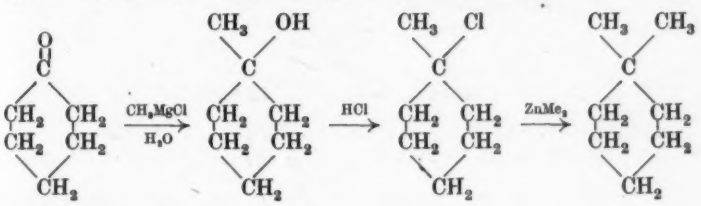
Linstead and Hibbitt[51] used a method entirely different from those used previously. 2-Methylhepta-6-ene-2-ol was cyclized with syrupy phosphoric acid at 100° and the olefin hydrogenated using Adams catalyst.

The most recent mention of this compound was by Zelinsky and Losik.[52] They reduced 2 : 2-dimethyl*bicyclo*-(0 : 1 : 3)-hexane to 1 : 1-dimethyl-*cyclo*hexane using a nickel–asbestos catalyst.

None of the above methods were suitable for the preparation on a larger scale, as they were either too long, or gave poor yields, or used an inaccessible starting material. For the present preparation an entirely different method was used. All materials used were cheap and easily obtainable.

*Cyclo*hexanone was converted in 80 to 84 per cent yield to the tertiary carbinol, 1-methyl*cyclo*hexan-1-ol, by reaction with methylmagnesium chloride. The carbinol was converted into the tertiary chloride and the

latter brought into reaction with zinc dimethyl in tetralin solution. A 37 per cent yield of pure hydrocarbon was thus obtained.



1-*Methyl*cyclo*hexan*-1-*ol*.

120 g (5 g-atoms) of fine magnesium turnings and 800 cc of dry ether were placed in a 5-litre, three-necked flask, fitted with a stirrer and two large double-surfaced condensers placed in series. Methyl chloride was led into the ether through a wide tube entering the flask through the third neck. When the ether had become saturated (5 to 10 min), 2 to 3 cc of bromide in ether were added. A vigorous reaction set in.

When the reaction was complete, 600 cc of ether were added and the flask cooled in an ice–salt mixture. 440 g (4·5 moles) of *cyclo*hexanone in 500 cc of ether were added slowly over a period of five hours with efficient stirring. The mixture was allowed to stand overnight and the resulting thick paste decomposed by adding 750 cc of water, followed by 20 per cent sulphuric acid, the flask being water- or ice-cooled. The ether layer was siphoned off, the water layer extracted with ether, and the combined ether layers were washed, dried, and distilled. After the ether had been removed on a water bath, the carbinol was distilled under reduced pressure. B.p. 92 to 93°/100 mm, n_D^{20} 1·4592.

1-*Methyl*-1-*chloro*cyclo*hexane*.

The methyl*cyclo*hexanol was shaken with excess of concentrated hydrochloric acid (1 mole : 3 moles) for five minutes. The mixture was allowed to stand for ½ hour and the upper layer separated and cooled in a freezing mixture. Gaseous hydrogen chloride was then passed through the crude chloride to convert the remaining carbinol. After washing and drying the liquid was distilled, giving a 77 per cent yield of the chloride. B.p. 83°/107 mm, n_D^{20} 1·4570.

The coupling reaction with zinc dimethyl was carried out in tetralin solution by our standard technique.

The product was fractionated and found to contain a considerable amount of 1-methyl*cyclo*hexa-1-ene (b.p. 109·5°). The fractions were combined and hydrogenated for seven hours at 140° and 100 atm pressure of hydrogen, using Raney nickel as a catalyst. The olefin was thus reduced to methyl*cyclo*hexane, the lower boiling point of which (b.p. 100·3°) enabled it to be separated more easily from the required hydrocarbon.

The mixture of methyl*cyclo*hexane and 1 : 1-dimethyl*cyclo*hexane thus produced was separated into its components by distillation through a Stedman column of 25 theoretical plates.

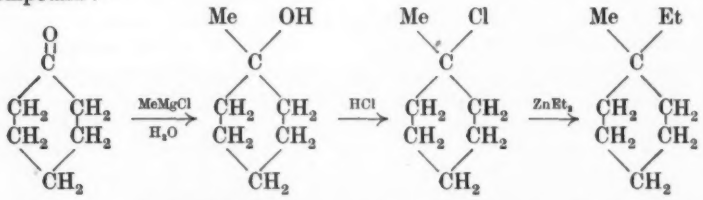
A yield of 37 per cent (based on the halide) of pure 1 : 1-dimethyl*cyclo*-

hexane was obtained having b.p. 119·2°/760 mm (corr.), n_D^{20} 1·4293. The best figures given by the A.P.I. for these two physical properties are 119·50° and 1·4293 respectively.

B. B. E.
E. J. F.

1-Methyl-1-ethyl*cyclo*hexane.

No reference to this compound has appeared in the literature. It was prepared by a similar method to that used for the 1 : 1-dimethyl compound :—



1-*Chloro*-1-*methyl*cyclo*hexane*, prepared as before from *cyclo*hexanone was coupled with zinc diethyl solution in tetralin by our standard technique. The product was fractionated first through a 60-cm Dufton column and then through a Stedman column of 25 theoretical plates; the first fractions obtained boiled mainly at 103 to 104°. From the boiling point we deduce that this was a mixture of methyl*cyclo*hexane (b.p. 100·3°) and 1-methyl-*cyclo*hexa-1-ene (b.p. 109·5°). The main fraction boiled at 151 to 152°. Redistillation gave a product of b.p. 151·1 to 151·3°, n_D^{20} 1·4418. Found: C, 85·36 per cent; H, 14·19 per cent. Methylethyl*cyclo*hexane requires C, 85·72 per cent; H, 14·28 per cent.

A lower boiling fraction of b.p. 147° was analysed. Found: C, 80·62 per cent; H, 13·60 per cent. It contained much oxygen, probably due to incomplete conversion of the carbinol into chloride. This fraction was heavily unsaturated due to methyl*cyclo*hexene, the presence of which should lower the boiling point of the mixture of carbinol and hydrocarbon.

B. B. E.
E. J. F.

1-Methyl-1-propyl*cyclo*hexane.

As with the methylethyl-homologue, no mention of this compound was found in the literature. The authors prepared it by a method analogous to that used for the *gem*-dimethyl compound, using zinc dipropyl in toluene. This solvent was used rather than tetralin, as the boiling point of the product was expected to be within 30° of that of the latter solvent, and separation would have been difficult.

1-Methyl*cyclo*hexane-1-ol was converted into the tertiary halide as before. Zinc dipropyl was made in the same way as zinc diethyl, and the apparatus for the coupling reaction was the same as that used for the previous preparation. The product was fractionated through a Stedman column. The main fraction representing a 28 per cent yield of the pure hydrocarbon had b.p. 174·3°/760 mm (corr.); n_D^{20} 1·4455. Found:

C, 85·3 per cent; H, 14·43 per cent; $C_{10}H_{20}$ requires C, 85·7 per cent; H, 14·3 per cent.

B. B. E.
E. J. F.

1 : 1-Diethyl*cyclo*hexane.

As with the two previous compounds no mention of this hydrocarbon occurs in the literature. The method used for the preparation was analogous to that used for the homologues.

1-*Ethyl*cyclo*hexan*-1-*ol* was prepared from *cyclo*hexanone and ethylmagnesium chloride in a yield of 80 per cent. B.p. 82 to 83°/24 mm.; n_D^{20} 1·4653.

1-*Ethyl*-1-*chloro*cyclo*hexane* was prepared by the method of Norris and Olmsted.[36] The reaction did not proceed as smoothly as for the methyl compound; difficulty was experienced in obtaining a specimen of the chloride free from carbinol and the yield was consequently low, 65 to 74 per cent; b.p. 73 to 74°/21 mm, n_D^{20} 1·4651; b.p. 96°/59 mm, n_D^{20} 1·4650. Found: Cl, 24·19 per cent; $C_8H_{15}Cl$ requires Cl, 24·21 per cent.

The coupling reaction was first carried out in tetralin solution. Owing, however, to the unexpectedly high boiling point of the required compound a good separation from the solvent could not be effected. No difficulty was encountered when toluene was used.

The product was distilled through a 30-cm Dufton column giving two main fractions. The lower fraction, boiling at 135°, contained mainly 1-ethyl*cyclo*hexa-1-ene, and the higher-boiling fraction the crude *cyclo*paraffin. The latter was redistilled through a Stedman column giving a yield of 34 per cent of pure 1 : 1-diethyl*cyclo*hexane, b.p. 179·3°/760 mm (corr.); n_D^{20} 1·4510. Found: C, 85·57 per cent; H, 14·2 per cent; $C_{10}H_{20}$ requires C, 85·7 per cent; H, 14·3 per cent.

B. B. E.
E. J. F.

1 : 2-Diethyl*cyclo*hexane.

The preparation of this compound, which is not described in the literature, was undertaken in view of the possible dehydrogenation to *ortho*diethylbenzene. Noller[9] had reported that he was unable to bring zinc alkyls into reaction with any of the secondary halides he tried. However, in view of the proximity of the secondary bromine atoms in 1 : 2-dibromo*cyclo*hexane and hence their more reactive nature, the reaction was attempted. The reaction proceeded smoothly in toluene solution at 80 to 90°, giving yields of about 15 per cent. A considerable quantity of high-boiling material was also present, and this was thought to be due to a Friedel-Crafts reaction between the solvent and the dibromide in the presence of the zinc bromide formed in the main reaction. Experiments were therefore made with *n*-heptane as the solvent when the yields rose to 20 per cent; the reaction did not proceed smoothly, however, and higher temperatures were found to be required. The dibromide partly disintegrated into *cyclo*hexane and *cyclo*hexadiene.

This appears to be the only example known of a reaction between a secondary halide and a zinc alkyl.

cyclo*Hexene* was obtained by dehydrating *cyclo*hexanol over activated alumina at 300°; an 80 per cent yield of product of b.p. 81 to 83° was obtained.

1 : 2-*Dibromo*cyclo*hexane* was prepared from *cyclo*hexene by the method of Snyder and Brooks.[53]

Substitution of bromine in the nucleus was avoided by keeping the temperature low and by using an excess of olefin.

The reaction was carried out in good daylight, a main fraction of b.p. 108 to 112°/25 mm being obtained, representing a yield of nearly 95 per cent. (Lack of sunlight was not found to reduce the yields by any appreciable amount.)

The coupling reaction : (a) *in toluene.*

A smaller version of the coupling apparatus was set up. After it had been filled with carbon dioxide, a known amount of zinc diethyl in toluene solution was poured into the flask and slowly heated to 60°, and 1 cc of undiluted dibromide added. On heating to 90° and dropping in more dibromide the temperature was observed to rise and gases were evolved. Stirring was then begun, and undiluted dibromide was added at such a rate that the temperature remained near 90°. The reaction was found to proceed slowly at 70°, or when diluted dibromide was used, at 90°.

On distillation the crude 1 : 2-diethyl*cyclo*hexane came over at 174 to 176° followed by a larger amount of higher-boiling material at 260°.

(b) *in* n-*heptane.*

To ensure that all the dibromide had reacted, the liquid was refluxed for a few minutes after each 10-g addition of the dibromide. The reaction was carried out using 1¼ moles of dibromide, and the product worked up in the usual way and distilled; the following fractions were collected :—

(1) 73– 98°	30 cc (*cyclo*hexene and *cyclo*hexadiene).
(2) 98–100°	140 cc *n*-heptane.
(3) 100–145°	45 cc *n*-heptane and ethyl*cyclo*hexene.
(4) 145–178°	15 cc.
(5) 178°/770 mm . . .	40 cc 1 : 2-diethyl*cyclo*hexane.

In spite of using an excess of zinc diethyl a trace of dibromide always remained. Sodium and potassium (under nitrogen) proved ineffectual in removing it. Refluxing with quinoline led to the formation of bromo-*cyclo*hexene, which could not be removed effectively from the required compound.

The method used eventually was to reflux the liquid with a 20 per cent solution of alcoholic potash for six hours. Crossley [54] found that in addition to potassium bromide ethyl *cyclo*hexa-1-enyl ether was also formed. The unsaturated ether was removed by shaking the product with concentrated sulphuric acid; four shakings were necessary.

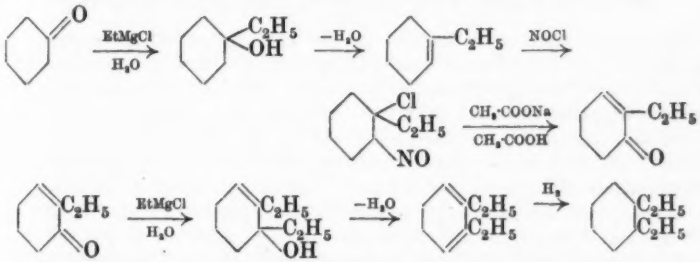
The product was fractionated through a Stedman column. The main fraction boiled at 177·6°/760 mm (corr.); n_D^{20} 1·4478. Found : C, 85·53 per cent; H, 14·38 per cent; $C_{10}H_{20}$ requires C, 85·7 per cent; H, 14·3 per cent.

Dehydrogenation of 1 : 2-diethyl*cyclo*hexane was undertaken, using a

platinized asbestos catalyst prepared by Zelinsky's method.[55] After passing the naphthene over the catalyst once, its refractive index was increased from 1·4478 to 1·4660. No further increase was observed after a second pass. This comparatively small increase indicated only partial dehydrogenation. The reason for this was clear, when spectroscopic examination revealed the presence of a considerable quantity of 1 : 1-diethyl*cyclo*hexane in the original sample.

The formation of 1 : 1-diethyl*cyclo*hexane could have occurred either in the course of the dibromo*cyclo*hexane–zinc alkyl reaction or during the shaking of the compound with conc sulphuric acid to remove unsaturated material. The former possibility was indicated when a spectroscopically pure specimen of the 1 : 2-diethyl compound (prepared by an unequivocal method) was shaken for several hours with conc sulphuric acid. No change in the refractive index was noted. The dehydrogenation of this pure specimen will be described elsewhere.

Pure 1 : 2-diethyl*cyclo*hexane was prepared as follows :—



1-Ethyl*cyclo*hexan-1-ol was obtained in 80 per cent yield from *cyclo*hexanone and ethyl magnesium chloride. Dehydration of the carbinol, by passing it over activated alumina at 200 to 220°, produced the olefin, 1-ethyl*cyclo*hexa-1-ene, b.p. 136·4°/760 mm, n_D^{20} 1·4570, in 85 per cent yield. The nitrosochloride of the olefin was prepared by Wallach's method [56] using amyl nitrite and hydrochloric acid in acetic acid at − 10°. Yields varied from 59 to 63 per cent. Decomposition to 2-ethyl*cyclo*hexa-2-enone was brought about by adding the nitrosochloride to a boiling solution of anhydrous sodium acetate in glacial acetic acid.[57] The yields of the ketone, b.p. 93 to 95°/30 mm, n_D^{20} 1·4824, never exceeded 45 per cent. (Semicarbazone, found, N, 23·17; calc 23·2 per cent.) This ketone was converted to the tertiary carbinol, 1 : 2-diethyl*cyclo*hexa-2-en-1-ol by ethyl magnesium chloride. On distilling the carbinol under 21 mm pressure partial decomposition occurred. The resulting organic layer was distilled under reduced pressure with a few crystals of iodine to complete the dehydration. After washing the olefin with sulphurous acid and dilute sodium bicarbonate solution, it was distilled under reduced pressure from sodium and then under normal pressure. The following constants were obtained for 2 : 3-diethyl*cyclo*hexa-1 : 3-diene : b.p. 173 to 174°/760 mm and 98°/60 mm, n_D^{20} 1·4812.

Analysis gave the following figures : Found : C, 88·1; H, 11·73 per cent; $C_{10}H_{16}$ requires C, 88·24; H, 11·76 per cent.

Hydrogenation of the diene was undertaken using a Raney nickel catalyst. One double bond was reduced at room temperature and 100 atm, the other was reduced at 180° and 140 atm. The product, after washing three times with water and drying over sodium sulphate, was distilled from sodium. A main fraction b.p. 176·8°/763 mm was collected. Its refractive index n_D^{20} was 1·4471.

Analysis of this fraction gave the following figures : Found : C, 85·69; H, 14·37 per cent : $C_{10}H_{20}$ requires C, 85·7; H, 14·3 per cent.

Spectroscopic examination showed no trace of the 1 : 1-diethyl isomer. Final constants for 1 : 2-diethyl*cyclo*hexane were found to be : b.p. 176·7°/760 mm, n_D^{20} 1·4471. Preliminary experiments on this synthesis were carried out by Mr B. P. Abel.

B. B. E.
E. J. F.

The High-boiling Products from Zinc Alkyl Reactions.

The xylene used as a solvent in the preparation of *neo*pentane was distilled at the end of each complete operation with a view to its re-use. It was noticed that in all cases there was a residue of b.p. higher than 144°. On investigation this was found to give mainly a product of b.p. 214°, which was saturated to permanganate. It is suggested that this is a mixture mainly of 1 : 3-dimethyl-4-*tert*-butylbenzene and 1 : 3-dimethyl-5-*tert*-butylbenzene with the former in excess, formed by a Friedel-Crafts reaction between xylene and *tert*-butyl chloride in the presence of zinc chloride.

Nightingale and Smith [58] have shown these isomers to be the more readily formed, and also that under the influence of the Friedel-Crafts catalyst the 1 : 3 : 5-substituted compound isomerizes to the 1 : 3 : 4-derivative.

The boiling point and refractive index of a fraction obtained at 210 to 214° corresponded to the figures given by Nightingale and Smith for 1 : 3-dimethyl-4-*tert*-butylbenzene, and it is suggested that the product obtained consisted mainly of this hydrocarbon : fraction 210 to 214°, n_D^{20} 1·4909; 1 : 3-dimethyl-4-*tert*-butylbenzene, (*a*) 86°/12 mm, (*b*) 200 to 214°; n_D^{20} 1·4909. The fractions, however, would not solidify in a container of solid carbon dioxide. The identity of this compound is by no means certain, spectroscopic evidence suggesting the alkyl groups to have mainly a 1 : 3 : 5-orientation.

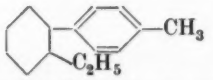
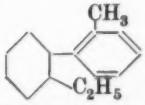
The tetralin residues from the preparation of 1 : 1-dimethyl*cyclo*hexane were also distilled; after the tetralin had come over a small residue resulted. This was distilled under reduced pressure and a fraction b.p. 180 to 190°/13 mm was obtained. It was viscous, almost colourless, and had a faint, pleasant smell.

To test the possibility of a Friedel-Crafts reaction due to the halide (1-methyl-1-chloro*cyclo*hexane) and the solvent (tetralin) in the presence of anhydrous zinc chloride, a small quantity of the halide, tetralin (in excess), and zinc chloride were heated for 8 hours. The product was distilled at 12 mm. Tetralin came over between 80 and 85° followed by a fraction, b.p. 180 to 190°. This fraction was viscous, light yellow, with

a bluish-green fluorescence. In no case, however, could a compound with a constant boiling point be obtained.

More definite results were obtained from the reaction between 1 : 2-dibromo*cyclo*hexane and zinc diethyl using toluene as a solvent. The high-boiling residue was distilled and two products were found. One boiled at 135°/20 mm and the other at 210°/15 mm. The lower-boiling fractions were redistilled at normal pressure using an airbath. A main fraction was obtained, b.p. 260 to 261°, n_D^{20} 1·5159. Found : C, 89·23 per cent; H, 10·73 per cent.

A suggestion capable of accounting for the high percentage of carbon and the smokiness of the flame when the compound was tested for halogen by Beilstein's method was one involving an aromatic ring :—

Either  or 

{$C_{15}H_{22}$ requires C, 89·11 per cent; H, 10·89 per cent}

This fits the requirements of the analysis very well. To test the suggestion, the material was hydrogenated with Raney nickel as catalyst. At 180° and 120 atm practically no reduction occurred. At 280° and a maximum pressure of 180 atm the reduction was complete. Found : C, 86·4 per cent; H, 13·2 per cent; $C_{15}H_{28}$ requires C, 86·54; H, 13·45 per cent. The b.p. 260° was practically identical with that of the starting material, but the refractive index was considerably lower, n_D^{20} 1·4844.

To find the position of the methyl group in the toluene ring, the unreduced material was oxidized with 5 per cent permanganate solution.

If coupling had taken place in the *para*-position, terephthalic acid would result on oxidation. If coupling had taken place in the *ortho*-position the compound would yield phthalic acid.

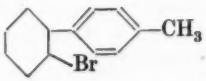
The product found did not melt below 360°; phthalic acid melts at 195° with decomposition.

The higher-boiling material, b.p. 210°/15 mm could not be identified. The analysis was identical with that of the above compound, but its molecular weight in camphor was 378. This molecular weight can be regarded only as approximate and this material may be a dimeride of the first compound ($C_{15}H_{22}$, M.W. 202), though how dimerization could occur is not clear.

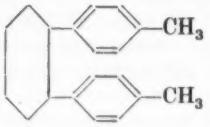
To find out how a Friedel-Crafts reaction between 1 : 2-dibromo*cyclo*hexane and toluene proceeded, the former was refluxed with an excess of toluene for 24 hours in the presence of zinc chloride.

No constant-boiling material was obtained. A fraction 130 to 140°/20 mm was analysed. Found : C, 75·84 per cent; H, 9·42 per cent; Br, 14·74 per cent.

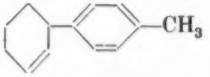
The refractive index was high, n_D^{20} 1·5346. The presence of bromine in the material could be accounted for by the formation of :—

 {Calc Br, 31·6 per cent}

The analytical figures would therefore indicate that the fraction contained about 50 per cent of this compound in which only one of the bromine atoms reacted with toluene, and 50 per cent of the compound in which both bromine atoms have reacted :—



An unsaturated compound :—



may also be present. This would account for the low percentage of hydrogen.

Collected Table of Physical Properties.

Hydrocarbon.	n_D^{20}.		B.p., ° C/760 mm.	
	This work.	A.P.I. Project 44, Selected values, 1945.	This work.	A.P.I. Project 44, Selected values, 1945.
2 : 2-dimethylpropane . .	—	—	9·5	9·50
2 : 2-dimethylpentane . .	1·3821	1·38217	79·0	79·205
3 : 3-dimethylpentane . .	1·3911	1·39090	85·8	86·071
2 : 2-dimethylhexane . .	1·3934	1·39349	106·9	106·843
3 : 3-dimethylhexane . .	1·4004	1·40009	111·9	111·972
2 : 3 : 3-trimethylpentane .	1·4076	1·4079	114·6	114·763
3-methyl-3-ethylpentane . .	1·4080	1·40775	118·05	118·262
2 : 3 : 3-trimethylhexane . .	1·4149	1·4143	136·8	138
3 : 3-diethylpentane . .	1·4203	1·4205	145·7	146·5
3 : 3-diethylhexane . . .	1·4246	—	166·2–166·3	—
3-methyl-3-ethylheptane . .	1·4208	—	163·7–163·9	—
1 : 1-dimethyl*cyclo*hexane .	1·4293	1·42890	119·2	119·5
1-methyl-1-ethyl*cyclo*hexane .	1·4418	—	151·1–151·3	—
1-methyl-1-propyl*cyclo*hexane .	1·4455	—	174·3	—
1 : 1-diethyl*cyclo*hexane .	1·4510	—	179·5	—
1 : 2-diethyl*cyclo*hexane . .	1·4471	—	176·7	—

ACKNOWLEDGMENT.

We wish to thank Sir Robert Robinson, P.R.S., for his interest in the research. This work has been carried out in collaboration with the Research Station of the Anglo-Iranian Oil Co. Ltd., and we acknowledge in particular the helpful advice of Dr D. A. Howes and Dr S. F. Birch. Thanks are due to the chairman of the Anglo-Iranian Oil Co. Ltd., for permission to publish the results, and also for financial support for the investigations. We also wish to thank Dr H. W. Thompson, F.R.S., for the spectroscopic examination of our hydrocarbons.

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OBITUARY.

COLONEL HENRY EDWARD MEDLICOTT, D.S.O.

HENRY EDWARD MEDLICOTT, who died at Nairobi on April 11, 1948, was born on July 24, 1882, and was a well-known figure in the petroleum industry. He became an Associate of the Institute in 1926 and a Fellow in 1939.

In 1926 he joined the Anglo-Iranian (then Anglo-Persian) Oil Co. to form and head its General Department, the function of which was to collect and disseminate, both within and without the company, information regarding the company's operations and the petroleum industry generally. This involved contact and liaison activities of a wide nature and in 1929 Colonel Medlicott was appointed a deputy-director of the company. Although he gave up management of the General Department at the beginning of 1947, Colonel Medlicott remained in close touch with it to the end.

Colonel Medlicott had also a brilliant military career and served his country in four wars. First, he saw service in the South African Campaign with the Irish Horse. In the First World War he served with distinction, was mentioned in despatches, and was awarded the D.S.O. and the French and Belgian Croix de Guerre. In the Afghan operations of 1919 he was again mentioned in despatches. When the Second World War broke out he rejoined the Army and was in France with the B.E.F. in 1940, whereafter he was a leading figure in the formation of the Petroleum Warfare Department and became its Deputy Director-General.

As "A.C." wrote in *The Times*: "A remarkably large and affectionate circle of friends and admirers mourns the death of 'Hal' Medlicott. Soldierly, sporting, and business knowledge and ability had made him as welcome and well-known as his infectious laugh almost everywhere between California and Calcutta."

A tribute from "E. F. R." reads:—

"Hal Medlicott or 'The Colonel,' as he was affectionately known by a host of friends, was a man of considerable charm, and, above all, a great Britisher. Nobody had a greater love of his country than Medlicott and there was nothing he would not do to further what he considered was its best interests.

"I had the pleasure of working with him for some twenty-six years. We were not only colleagues, but we were very firm friends; indeed it was difficult to know Medlicott and be otherwise.

"Much of his time was perforce spent in London, but he was, at heart, essentially a country gentleman and he was never happier than when he was spending his leisure among his horses and dogs, for which he had the greatest affection. The loss of an eye in a hunting accident, which meant that henceforth he would have to forsake the hunting field, was a very bitter blow to him and yet he showed at that time an example of tremendous courage in his great disappointment.

"In his business activities he was always colourful, but I prefer to think of him as someone who never quite lost his ability to retain a goodly part of his youth. He enjoyed every minute of his life, which was full of interest, and his great courage was in evidence throughout the last years when he suffered greatly from asthma. Never once did he complain about his illness.

"Many people will know of the part he played in the oil industry but few will have any knowledge of the many kindly things he did during his life to help those who had found life hard. His activities in connexion with the British Legion after the First World War were manifold; many an unfortunate ex-serviceman was helped to start a new life and very few knew of the efforts made and financial assistance given by Medlicott in this connexion. I think perhaps the truest thing one can say of him is that he was a very human person who was much loved by all his friends."